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Geochemistry of Carbonate Sediments and Sedimentary Carbonate Rocks

Part I Carbonate Mineralogy Carbonate Sediments

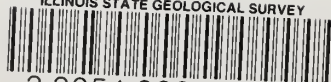
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**GEOCHEMISTRY OF CARBONATE
SEDIMENTS AND SEDIMENTARY
CARBONATE ROCKS**

Part I

**Carbonate Mineralogy
Carbonate Sediments**



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FOREWORD

Detailed knowledge of the chemical and mineralogical variations that exist in the carbonate rocks limestone and dolomite and of the processes responsible for this diversity is fundamental to the Illinois State Geological Survey's program of furthering the practical utilization of these natural resources of the state. Chemical composition is particularly important when the rocks are used as agricultural limestone and fluxing stone or in the manufacture of dolomite refractories, lime, calcium carbide, sodium carbonate, glass, and other products.

The invitation extended to Dr. Graf by the United States Geological Survey to prepare the chapter on sedimentary carbonates for their revision of F. W. Clarke's "Data of Geochemistry" has afforded a valuable opportunity for the state and federal geological surveys to cooperate in a basic review of selected topics in carbonate geochemistry. The resultant material is presented in five Illinois State Geological Survey Circulars and subsequently will serve as the basis for a condensed treatment in the revised "Data of Geochemistry."

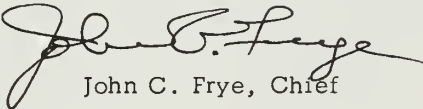
Part I, published as Circular 297, includes an introduction and sections on carbonate mineralogy and carbonate sediments.

Part II, Circular 298, includes the section on sedimentary carbonate rocks.

Part III will deal with the distribution of minor elements.

Part IV will present isotopic composition, present chemical analyses, and also will contain the bibliography for the first four circulars.

Part V, concerned with aqueous carbonate systems, will be published at a later date.



John C. Frye, Chief

GEOCHEMISTRY OF CARBONATE SEDIMENTS AND SEDIMENTARY CARBONATE ROCKS

Part I: Carbonate Mineralogy — Carbonate Sediments

Donald L. Graf

ABSTRACT

The distribution of major and minor elements in sedimentary carbonate rocks and the mechanisms responsible for this distribution are considered on the basis of published information contained in geologic studies, and in studies of present-day environments of carbonate deposition, isotopic composition of carbonates, and experimental aqueous and nonaqueous carbonate systems. There are five parts in the series, and an extensive bibliography appears in Part IV.

INTRODUCTION

The discussion which follows is concerned with carbonate rocks, chiefly limestone and dolomite and their unconsolidated equivalents, which have not been subjected to hydrothermal or metamorphic environments. Some discussion of sedimentary magnesite-, siderite-, and rhodochrosite-bearing materials is also included.

Limestone is defined for convenience as a consolidated sedimentary rock containing more than 50 percent of the minerals calcite (plus aragonite) and dolomite (including ferroan dolomite) in which calcite (plus aragonite) is more abundant than dolomite (including ferroan dolomite) (see Rodgers, 1954). Dolomite (the rock) is similarly defined, but with dolomite (including ferroan dolomite) more abundant than calcite (plus aragonite). The arbitrary 50 percent limit obviously excludes some rocks in which calcite and dolomite together constitute the most important single constituent.

There appears to be no general agreement on quantitative systems of nomenclature for impure carbonate rocks, for rocks made up of mixtures of calcite and dolomite, and for dolomites (the mineral) containing various amounts of Fe in solid solution. Descriptive terms for these materials are used here in a qualitative sense. For example, an argillaceous limestone is one containing an appreciable amount, but less than 50 percent, of clay minerals. Whenever possible the terms are referred to chemical and mineralogic analyses for further definition in specific contexts.

Similarly, the use of such adjectival modifiers as ferroan and magnesian in describing carbonate solid solutions is qualitative. Terms such as "ankerite" and "mesitite" for arbitrary compositional ranges have but little theoretical justification in the absence of evidence for structural discontinuities in these solid solution series. Perhaps even more important, the use of these terms has not contributed significantly to petrologic understanding as have, for example, the arbitrary divisions of the albite-anorthite series.

Carbonate sediments considered as a whole are noteworthy in that material produced through the activity of organisms appears to be the greatest single com-

ponent. The character of carbonate sedimentation is governed more forcibly by topography and the consequent detrital contribution, and by climate and other factors that affect water chemistry and biologic activity, than it is by its position in an epeirogenic or geosynclinal area. Indeed, if the rate of deposition is sufficient to keep up with the rate of subsidence of geosynclines, great thicknesses of shallow-water limestones may accumulate. Sloss (1947) contrasts the 26,000 feet or more of Oquirrh Limestone of Pennsylvanian-Permian age in western Utah with the few hundred feet of its platform equivalent in central Utah. Dunbar and Rodgers (1957) noted that most of the sediments of the Appalachian geosyncline are shallow-water, indicating that deposition kept up with the rate of sinking. The platform-type carbonate sediments of the present-day Persian Gulf also are accumulating in a geosynclinal series.

The carbonate portion of carbonate rocks consists of mixtures in various proportions of detrital terrigenous carbonate particles, reworked fragments of penecontemporaneous carbonate sediments, oolites, fecal pellets, and skeletal material, all cemented by microcrystalline ooze and coarser grained, pore-filling cement (see Folk, 1959). The rocks may contain replacive dolomite in addition to that found in some places as an originally precipitated ooze. A distinction as to the vigor of waves and currents in the depositional environment, based on the amount of interstitial microcrystalline carbonate matrix remaining, appears to be generally valid (Bramkamp and Powers, 1958; Carozzi, 1960, p. 226; Nelson, 1959), although it has been suggested that in some rocks this matrix has recrystallized to clear calcite cement.

Noncarbonate minerals may be detrital or organically or inorganically formed during or after deposition. Terrigenous contributions probably dilute to an unusual degree carbonate sediments now being formed, because of the greater-than-average topographic relief of the continents.

Limestones are particularly susceptible to post-depositional recrystallization and carbonate cementation that may obscure evidence regarding the manner of their formation. Illing (1954) has noted that recrystallization to microcrystalline limestone, obliterating fossils and individual oolites, is already taking place in the Bahamas early in diagenesis. Considerable depletion or enrichment of CaCO_3 may occur as well, so that it is somewhat arbitrary to consider carbonate sediments containing more than 50 percent carbonate minerals to be the unconsolidated equivalents of carbonate rocks.

In the sections that follow, the composition and distribution of carbonate sediments from various present-day environments are described, and an attempt is made to relate lithified carbonate rocks to their original environments of deposition. This treatment leads to a considerable emphasis upon the processes and mechanisms responsible for the required 50 percent or more carbonate content, for the presence in some carbonate rocks of other major constituents such as silica and bituminous matter, and for the observed minor-element distributions. The usefulness of geochemical data for other than gross averages must ultimately rest upon thorough understanding of process.

The chemical information available at present is seldom adequate to define the depositional environment of a given carbonate rock, particularly if it is a very pure limestone. The isotopic compositions of coexisting sedimentary minerals and the concentrations of minor elements such as boron in accessory minerals are most useful, but this information is not yet available for many samples. In most cases where it seems that the depositional environment can be defined with some confidence, heavy emphasis has been placed upon such criteria as texture

and fossil content. In spite of the use of such additional nonchemical criteria, the degree to which environmental identification can be made varies greatly, and a mixed classification in the discussion of sedimentary carbonate rocks has resulted. Thus the headings "cave deposits" and "shallow-water marine limestones" (oolites, reefs, coquinas, chemically precipitated CaCO_3) have rather definite environmental connotation, but "fine-grained limestones" and "phosphatic limestones" refer to textural and chemical types of carbonate rocks that probably come from a variety of environments.

At the present state of knowledge, one value of a summary of this sort is the mere listing of carbonate rocks whose depositional environment is believed to be known. They then may be studied further and an attempt made to formulate geochemical criteria for recognition of environments. Although most carbonate rocks probably were formed in relatively shallow, well aerated marine waters receiving but little terrigenous detritus, it is vitally important, for an understanding of the range of operative processes, that the environments of formation of less common carbonate rock types, such as some of those discussed here, be investigated.

CARBONATE MINERALOGY

The most important rock-forming carbonate minerals are two rhombohedral compounds, calcite (CaCO_3) and dolomite ($\text{CaMg}(\text{CO}_3)_2$), that are found widely distributed in sedimentary, metamorphic, and hydrothermal environments. Dolomite is a 1:1 ordered compound—that is, its crystal structure differs from that of calcite in having successive basal cation planes populated exclusively by each of the two kinds of cations in turn. Three other calcite-type rhombohedral carbonates, magnesite (MgCO_3), siderite (FeCO_3), and rhodochrosite (MnCO_3), occur only in restricted types of sedimentary rocks but are found rather commonly in hydrothermal assemblages. Kutnahorite ($\text{CaMn}(\text{CO}_3)_2$) has the dolomite-type structure and has been described by Frondel and Bauer (1955) from the Mn-rich orebody at Franklin, New Jersey, and from two localities in Czechoslovakia. It is of interest principally because its behavior in experimental studies has furthered understanding of the properties of carbonate solid solutions. Aragonite, the orthorhombic polymorph of CaCO_3 , is a common constituent of geologically young materials, including oolites, cave and spring deposits, and invertebrate skeletal remains.

Compilations of chemical analyses of carbonate minerals such as those made by Bilibin (1927) and Ford (1917) are of limited usefulness because they do not consider composition-temperature relationships and because the materials analyzed may have contained more than one phase. Palache et al. (1951) discussed the physical properties of the carbonates, Graf and Lamar (1955), the physical properties of the Ca and Mg carbonates only. Goldsmith (1959) has reviewed recent work on the phase relations of the anhydrous carbonates.

CALCITE-TYPE STRUCTURES

The cations Fe^{++} , Mg^{++} , and Mn^{++} have closely similar ionic radii, and chemical analyses of supposedly single-phase materials suggest that extensive solid solution between MgCO_3 and MnCO_3 and complete solid solution between the other two pairs is possible (Palache et al., 1951; Frondel and Bauer, 1955). Relatively pure end members may be formed, of course, in natural environments that are essentially free of possible substituting ions. Thus, a magnesite concentrate from the anhydrite zone of the Middle Evaporite Bed, in northeast Yorkshire, contains only 0.17 percent Fe and 0.02 percent Mn (D. L. Graf, unpublished data).

Ca^{++} is sufficiently larger than Mg^{++} , Mn^{++} , and Fe^{++} so that solid solution between CaCO_3 and the carbonates of these three cations is incomplete at earth-surface temperatures. Goldsmith and Graf (1957) found that a complete series of solid solutions exists between calcite and rhodochrosite above approximately 550°C , but that at lower temperatures a gap exists in the Mn-rich half of the system. At 450°C , the lowest temperature at which equilibrium could be reached in experimental runs, the gap extends from about 52 to about 80 mol percent MnCO_3 . This range is in reasonable agreement with the gap observed by Frondel and Bauer (1955) in their frequency distribution of Ca-Mn carbonates from Franklin, New Jersey, based upon chemical analyses and optical determinations. Goldsmith and Graf precipitated the complete series of Ca-Mn carbonate solid solutions at room temperature, and at least those compositions lying below the solvus described above must have been metastable.

At 500°C , approximately 14 mol percent FeCO_3 can be taken into solid solution by calcite and about 5 mol percent CaCO_3 by siderite (Rosenberg and Harker, 1956). At 700°C some 37 mol percent FeCO_3 can be taken up by calcite (Goldsmith, 1959). The solubility of FeCO_3 in calcite is thus between those of MgCO_3 and MnCO_3 . Information on natural materials is limited to chemical analyses (see, for example, Palache et al., 1951), which indicate that substitutions of a few mol percent of either carbonate for the other are not uncommon. Larger substitutions are suggested by a few analyses.

The immiscibility gap in the system CaCO_3 - MgCO_3 between magnesite and dolomite is virtually complete. At 900°C magnesite will take only about 2 wt percent CaCO_3 into solid solution (Harker and Tuttle, 1955), and dolomite will take only about 1 percent excess MgCO_3 (Goldsmith, 1959). Dolomite will, however, hold about 2 mol percent excess CaCO_3 at 800°C and 4 mol percent excess at 900°C (J. R. Goldsmith, unpublished data). The allowed substitution at a given temperature of a greater excess of the larger Ca^{++} ion in dolomite, compared with the allowed excess substitution of Mg^{++} , cannot be explained by simple considerations of ionic size. The solubility of MgCO_3 in calcite in equilibrium with dolomite rises from 5.5 mol percent at 500°C to 17.5 mol percent at 800°C (Harker and Tuttle, 1955; Graf and Goldsmith, 1955, 1958). The equilibrium solubility of MgCO_3 in calcite in equilibrium with $\text{MgO} + \text{CO}_2$, which is a function of both temperature and partial pressure of CO_2 , also has been measured by Graf and Goldsmith.

The Mg content of a number of naturally occurring calcites has been determined (Chave, 1954a; Goldsmith et al., 1955; Graf and Goldsmith, 1958). Tufa from Mono Lake, California, contains up to $2\frac{1}{2}$ mol percent MgCO_3 in solid solution, and calcite from the low temperature hydrothermal magnesite orebody at Currant Creek, Nevada, contains 6 mol percent. The magnesian calcites making up the hard parts of some invertebrates contain as much as 18 mol percent MgCO_3 and are thus clearly metastable after the death of the organism, whatever the biochemical conditions were within the organism when the magnesian calcite was laid down. Also metastable at the conditions under which they formed are the magnesian calcites reported by Alderman and Skinner (1957) to be precipitating in ephemeral lakes and in the Coorong in southeastern Australia, and similar synthetic materials prepared at room temperature (Graf and Goldsmith, 1956; Brooks et al., 1950) and at elevated temperatures (Graf and Goldsmith, 1955, p. 124; Harker and Tuttle, 1955, p. 278).

Because magnesian calcites in sedimentary environments typically lose their Mg rather quickly with geologic time, the calcites from Mesozoic and older rocks are virtually free of Mg (Chave, 1954b; Goldsmith et al., 1955). Metastable magnesian calcite fossils may in rare instances persist over long geologic time if sealed

in relatively impermeable rocks. Heinz Lowenstam (personal communication) found calcitic Pennsylvanian coelenterates containing as much as 5.2 wt percent MgCO_3 and a Cretaceous coelenterate containing about 7 wt percent MgCO_3 .

Calcites in marbles have been observed to contain up to $7\frac{1}{2}$ mol percent MgCO_3 (Goldsmith et al., 1955; Graf and Goldsmith, 1958). When the rock contains dolomite in equilibrium with magnesian calcite, the amount of solid solution constitutes a geologic thermometer; thus $7\frac{1}{2}$ mol percent MgCO_3 corresponds to a temperature of about 600°C . If there is no dolomite present with the calcite, the temperature indicated is a minimum one, inasmuch as there may not have been enough Mg in the environment to saturate the calcite. It is not possible to specify a temperature of formation for predazzites, some of which have calcites containing up to $7\frac{1}{2}$ mol percent MgCO_3 , because the calcite was in equilibrium with $\text{MgO} + \text{CO}_2$ and actually may have increased in Mg content during cooling (see Goldsmith et al., 1955).

Some marbles contain dolomite plus two magnesian calcites of differing composition, and in a number of such rocks (Goldsmith et al., 1955; Goldsmith, 1956, 1957, and unpublished data) it has been possible to show by single-crystal X-ray diffraction methods that the dolomite and poorly magnesian calcite occur together in tiny blebs that have the same crystallographic orientation as do enclosing host crystals of more highly magnesian calcite, from which the blebs must have exsolved during cooling. In some cases such dolomite inclusions in milky metamorphic calcites are too small to be visible optically. It is probable that at least some coarser dolomite-calcite intergrowths and independent grain assemblages of these two minerals in marbles may have originated by exsolution and subsequent recrystallization (J. R. Goldsmith, personal communication). Oriented exsolved dolomite has been produced experimentally by heating to 500°C a single-crystal, echinoidal, magnesian calcite host containing some 10 mol percent MgCO_3 (Goldsmith, 1956).

Fine or even submicroscopic intergrowths from Franklin, New Jersey, consist of kutnahorite and either a more Ca-rich or a more Mn-rich carbonate, and single-crystal X-ray photographs show the crystallographic orientation of the two phases to be the same (Goldsmith, 1957; J. R. Goldsmith and D. L. Graf, unpublished data). These materials, if interpreted as exsolution products, indicate the presence of an immiscibility gap in the Ca-rich half of the system $\text{CaCO}_3\text{-MnCO}_3$, which it has not yet been possible to demonstrate experimentally because of slow reaction rates in the system at low temperatures.

The extent of cation substitution observed in natural calcites is a function not only of the supply of such ions in various environments and the extent to which they can be accommodated in the calcite structure, but also of the partial pressures of CO_2 required to maintain the solid solutions. Thus the high partial CO_2 pressures required to maintain ZnCO_3 at elevated temperatures (see Harker and Dutta, 1956) indicate that calcites containing significant amounts of ZnCO_3 would decompose at moderate temperatures to yield a more nearly pure calcite unless CO_2 pressures were high (Goldsmith, 1959). High-temperature calcites typically contain more Mg^{++} than Fe^{++} , although the solubility of Fe^{++} in calcite at a given temperature has been shown to be greater than that of Mg^{++} . Goldsmith suggests that decomposition relations may be the controlling factor here. The equilibrium thermal decomposition curve of siderite is not yet accurately known.

DOLOMITE-TYPE STRUCTURES

The formation of the 1:1 cation-ordered carbonate, dolomite, appears to be favored by a large difference in the ionic size of the two cations, and thus the failure to synthesize the compound $\text{CaFe}(\text{CO}_3)_2$ (Rosenberg and Harker, 1956; Goldsmith, 1959) or to find it in nature is puzzling.

The Fe^{++} found commonly in ferroan dolomites substitutes in Mg^{++} positions because of the similar ionic sizes of these two ions. Thus the formula $\text{Ca}_{1.025}\text{Mg}_{0.626}\text{Fe}_{0.330}\text{Mn}_{0.022}(\text{CO}_3)_{1.997}$ may be calculated from the analysis of a single-phase ferroan dolomite with an enlarged unit cell from a bed of nonmarine lamellibranchs in the Lancashire Coal Measures (Howie and Broadhurst, 1958; Broadhurst and Howie, 1958). Similarly, it may be noted from Frondel and Bauer's (1955) analyses that substitution of Fe^{++} and Mg^{++} in kutnahorite is accompanied by a greater decrease in Mn^{++} than in Ca^{++} .

A number of more complex dolomite solid solutions have been described. Hurlbut (1957) gives analyses of five dolomites from Tsumeb, Southwest Africa, that show up to 8.74 wt percent ZnO and up to 4.96 wt percent PbO. The results of differential thermal analysis can be correlated with change in composition of these materials, but there is a much less regular variation of indices of refraction, specific gravity, and unit cell dimensions.

Above about 650°C a complete series extends between $\text{CaMn}(\text{CO}_3)_2$ and $\text{CaMg}(\text{CO}_3)_2$ (Goldsmith and Graf, 1960), and order reflections are observed in X-ray powder patterns of compositions containing more than about 50 mol percent dolomite. The single phase that is stable at high temperatures is replaced at lower temperatures by two or more phases. Replacement of Mg^{++} by Mn^{++} in this series obviously cannot be nearly as extensive at low temperatures as the replacement of Mg^{++} by Fe^{++} in ankerite. Because Mn^{++} is significantly larger than Fe^{++} or Mg^{++} , it is possible that Mn^{++} may go into Ca^{++} positions to some extent.

The temperatures at which the several 1:1 compounds disorder vary greatly. Dolomite remains ordered at the temperatures up to 900°C from which it has thus far been quenched. Heating experiments using natural (ordered) kutnahorite single crystals show that the ordering temperature for $\text{CaMn}(\text{CO}_3)_2$ is at or below 450°C. The ordering reflections of this material are too weak to be detected with certainty in powder X-ray diagrams, and thus it is not known whether any of the synthetic materials of this composition prepared over a range of temperatures were ordered (Goldsmith and Graf, 1960). Although the considerable amount of FeCO_3 that has been experimentally substituted into calcite suggests that a disordered $\text{CaFe}(\text{CO}_3)_2$ could be produced at a sufficiently high temperature and partial pressure of CO_2 , this material would, on cooling, apparently break up into a CaCO_3 -rich phase and a FeCO_3 -rich phase rather than ordering.

As part of an experimental study of the subsolidus relations in the system CdCO_3 - MgCO_3 , J. R. Goldsmith (personal communication) has determined the ordering behavior of compositions near $\text{CdMg}(\text{CO}_3)_2$. These materials, not encountered in nature, have ordering temperatures intermediate to those of dolomite and kutnahorite, so that Goldsmith has been able to put together an unusually complete picture of ordering relations that is invaluable in understanding dolomite and kutnahorite.

As demonstrated in the CdCO_3 - MgCO_3 system, the 1:1 compounds may depart significantly from ideal composition and still show the extra X-ray reflections resulting from cation order. Natural kutnahorites from Franklin, New Jersey, con-

taining approximately 10 mol percent excess CaCO_3 in their structures still show some order when examined by single-crystal techniques. Goldsmith and Graf (1958) determined by X-ray diffraction the mol percent CaCO_3 in dolomites from various rocks, after verifying from emission spectrographic analyses that the amount of Fe and Mn in the samples was too small to affect significantly the unit cell size. The metamorphic and hydrothermal dolomites examined and most of the dolomites associated with evaporite deposits have essentially the 1:1 molar ratio of CaCO_3 : MgCO_3 . Dolomite occurring as scattered rhombs in Ordovician and younger limestones not uncommonly contains CaCO_3 above this ratio, reaching values as high as 56 mol percent CaCO_3 . A number of Cenozoic rocks from Florida made up almost entirely of dolomite show the same effect, as do dolomite from a Searles Lake horizon having a radiocarbon date of 10,000 years and the dolomite described by Alderman and Skinner (1957) as precipitating today in ephemeral lakes and in the Coorong in south-east Australia.

From the results of laboratory studies, sedimentary dolomites containing more than a fraction of one percent excess CaCO_3 must be metastable at earth-surface conditions. These dolomites are similar to the poorly ordered Ca-rich protodolomites produced synthetically by Graf and Goldsmith (1956) at temperatures below 200°C and in experimental runs of short duration at higher temperatures. The formation and persistence of protodolomites has been interpreted (Goldsmith, 1953; Graf and Goldsmith, 1956) as a consequence of the similarity in terms of crystal energy of the non-equivalent Ca and Mg positions. As a consequence, it is difficult, particularly at rapid rates of crystallization, either to produce initially a perfectly ordered array or to move cations later from wrong positions to stable positions of lower energy.

TERNARY SYSTEMS

The subsolidus relations in the system CaCO_3 - MgCO_3 - MnCO_3 , as determined from 500° to 800°C by Goldsmith and Graf (1960) using a squeezer-type apparatus, are summarized in figure 1. Phase diagrams at 600° and 700°C lie between those shown for 500° and 800°C , with two- and three-phase fields progressively decreased in area from those at 500°C . The existence of stable, sedimentary, three-phase rhombohedral carbonate assemblages in this system is indicated by the increase in area of the three-phase field with decreasing temperature, provided that hydrous phases do not intervene. At experimentally investigated temperatures below 600°C , manganoan dolomites contain less than 50 mol percent CaCO_3 .

Rosenberg (1959) reported the synthesis at 450°C of ferroan dolomites having up to 75 percent of the magnesium positions filled with iron, a figure in good general agreement with the maximum observed in natural samples. Dolomitic phases with 75 to 85 percent substitution were found by Rosenberg to lie in a three-phase region in equilibrium with calcite and siderite solid solutions. J. R. Goldsmith, D. L. Graf, and David Northrop (unpublished data) found no three-phase region in the system between 700° and 800°C .

ARAGONITE-TYPE STRUCTURES

Jamieson (1953) computed the pressure for calcite-aragonite equilibrium at 25°C , using available data, and then determined the equilibrium curve as a function of temperature and pressure over the range 25 to 80°C and several thousand kg/cm^2 , using the electrical conductivity of aqueous solutions of each form. MacDonald (1956) studied the equilibrium in the range 250 to 600°C and 6 to 30 kb, using the simple squeezer. Clark (1957) used an experimental apparatus in which pressure

was generated by compression of nitrogen and measured with a manganin coil. The data obtained by these several methods are in good agreement. Aragonite is the high pressure polymorph of calcite and is metastable at the temperatures and pressures near the earth's surface. Sedimentary aragonites in rare instances may be preserved for geologically long times if sealed in asphalt or highly impermeable rocks; Stehli (1956) described aragonite fossils from the Lower and Middle Pennsylvanian. The geothermal gradient lies completely in the calcite field, so only in peculiar local conditions of high hydrostatic pressure and moderate temperature would aragonite be stable at depth.

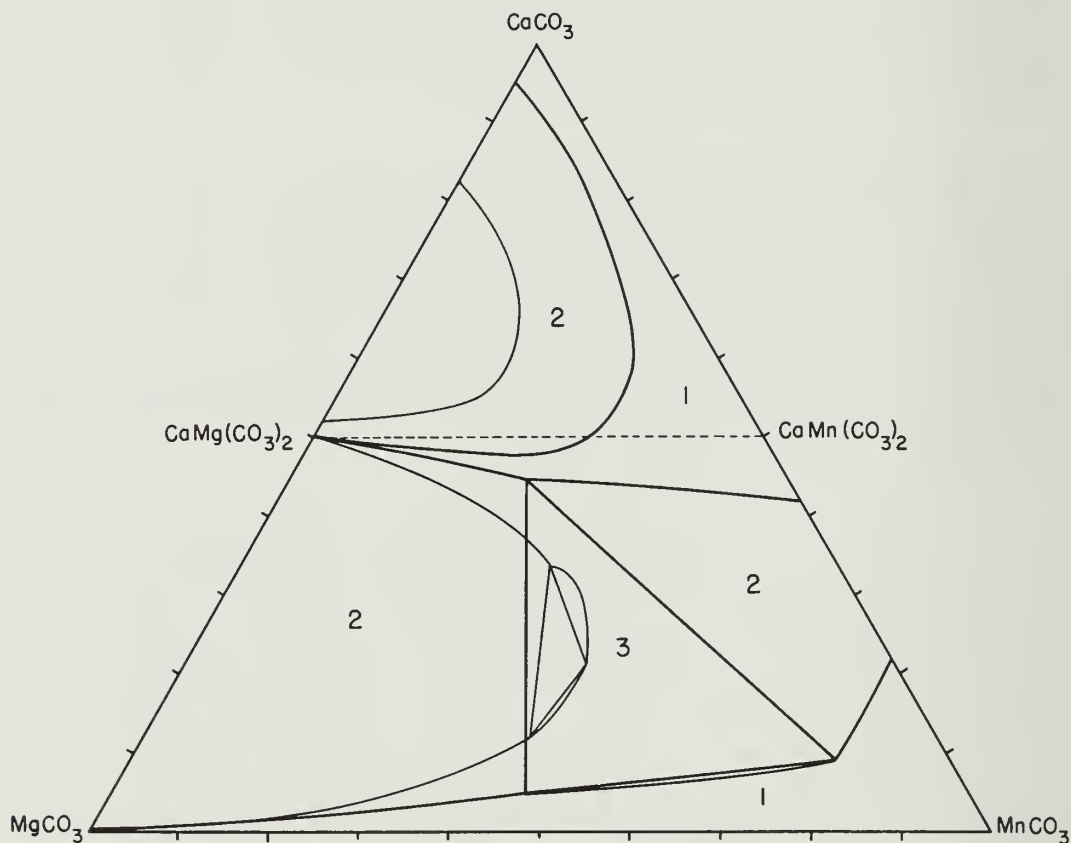


Fig. 1 - Subsolidus relations in the system $\text{CaCO}_3\text{-MgCO}_3\text{-MnCO}_3$, adapted from Goldsmith and Graf (1960). Heavy lines and numbers delimit the one-, two-, and three-phase regions at 500°C ; lighter lines show the analogous situation at 800°C . In this temperature range, at a pressure of 10 kb, all phases are rhombohedral.

The suggestion has been made (see Johnston et al., 1916) that the presence of foreign ions such as Pb^{++} and Sr^{++} in solid solution might stabilize aragonite with respect to calcite at earth-surface conditions. MacDonald (1956) assumed that CaCO_3 forms an ideal solid solution with other components and used the experimentally determined value of 200 ± 100 cal/mol for the difference in Gibbs

free energy between aragonite and calcite at 25°C to show that at least 30 percent of components other than CaCO_3 would be needed in aragonite to stabilize it relative to calcite. Palache et al. (1951) observed a maximum of 9 percent solid solution in natural aragonites.

Mg is even less soluble in the orthorhombic aragonite structure than in calcite. Goldsmith (1959) noted that even at 800°C, in an experimental system in which the calcite is saturated with MgCO_3 , aragonite takes no significant amount of Mg into solid solution. Both skeletal and inorganically precipitated marine aragonites contain only insignificant amounts of Mg; Chave (1954a) noted that the former seldom contain more than 1 percent MgCO_3 . Larger cations substitute in aragonite, however; Palache et al. (1951) cited chemical analyses indicating Sr:Ca as high as 1:25 and Pb:Ca as high as 1:12.

John Jamieson (personal communication) has prepared a complete series of orthorhombic solid solutions between CaCO_3 and SrCO_3 by rapid mixing of 0.1 M (Ca,Sr) Cl_2 and Na_2CO_3 solutions at 82.9°C. By heating these materials to temperatures above the aragonite-calcite transition in this system and then quenching them, Jamieson obtained single-phase calcite-type structures containing from 0 to 70 mol percent SrCO_3 . Faivre (1946) described synthetic orthorhombic calcium-barium carbonates containing up to 65 percent Ba and rhombohedral ones with up to 40 percent Ba. Some of the latter are anion-disordered.

MIXED-LAYERING

Both ordered and disordered rhombohedral carbonate solid solutions are frequently observed to have abnormal *c*-axis progressions, which Graf et al. (1957) have interpreted by using mixed-layer theory. The effect is characteristic of Ca-rich dolomites and highly ferroan dolomites. It also occurs in supposedly ideal disordered solid solutions involving cations differing considerably in size, such as Ca-Mn and Ca-Mg, in which the amount of substitution is considerable and some segregation of cation types into discrete planes or regions has taken place. These mixed-layered materials obviously do not fit into existing carbonate mineral classifications.

CRYSTAL ZONING

Crystal zoning parallel to rhomb faces is not uncommon in the rhombohedral carbonates. The angle between the rhomb faces and the basal planes involved in the mixed-layering just described is about 45°, and the two phenomena are quite distinct. Grout (1946) described zoned carbonates from hydrothermal environments, and a number of workers, using optical measurements and differential etching with acid, have reported calcite zones in sedimentary dolomite crystals.

Staining of Illinois Paleozoic limestones with K ferricyanide solution has shown in some instances that the Fe^{++} content of dolomite rhombs is concentrated in a number of sharply defined zones and is essentially absent in the others. The total amount of iron involved is not great; six concentrates of dolomite rhombs from these limestones contained from 0.46 to 1.06 percent Fe and from 0.032 to 0.120 percent Mn (Goldsmith and Graf, 1956).

Magnesite crystals described from a Permian halite bed of northeast Yorkshire have centers with markedly lower refringence than the rest of the crystal (Armstrong et al., 1951). Well formed zoned crystals of calcite, 0.1 to 0.2 mm in diameter, are reported in many samples from the North Atlantic deep-sea cores (Bramlette and Bradley, 1940).

A striking example of crystal zoning occurs in the Northampton sand ironstone of central England. The principal carbonate phase of the ironstone, described earlier on the basis of optical and chemical study as a siderite containing a total of about 20 mol percent MgCO_3 , MnCO_3 , and CaCO_3 in solid solution, was shown by Cohen (1952), using a microradiographic technique, to consist of zoned crystals having alterate layers of iron carbonate and iron-free carbonate. Although perhaps not generally recognized, such zones deserve to be considered individually, inasmuch as they represent responses to distinctly different chemical environments.

LUMINESCENCE

Certain energy levels in naturally occurring calcite and dolomite crystals can be populated with metastable electrons by exposure to Co^{60} gamma radiation or to the naturally occurring radiation in sedimentary environments. The thermoluminescence which results from heating natural materials previously exposed to Co^{60} radiation is released in four temperature regions, 120° to 140° , 150° to 190° , 210° to 250° , and 290° to 310°C (Daniels and Saunders, 1951). The two lower temperature peaks are not generally observed for natural materials run as received because ambient temperatures are high enough to drain electrons from the traps involved in this low temperature thermoluminescence. Zeller and Pearn (1960), however, observed the 125°C peak for naturally refrigerated Antarctic limestone samples and estimated a half-life of about 25 hours at 25°C .

Synthetic calcium carbonate with a low impurity level shows no radiation-induced thermoluminescence, unlike similar material crystallized in the presence of such impurities as Fe, Mn, Mg, Sr, or Ba (Zeller et al., 1955). The high-purity synthetic material ground in a mortar or compressed for 12 hours at about 700 kg/cm^2 (but not irradiated), gives a curve with maxima at 360° and 424°C (Debenedetti, 1958). Zeller et al. found that for limestone samples older than 100 million years the thermoluminescence induced by natural radiation is always decreased by application of pressur . Jamieson and Goldsmith (in press) attempted to estimate the localized temperatures and pressures generated within calcite during grinding, which converts this material to aragonite, the polymorph stable at somewhat higher pressures (see also Burns and Bredig, 1956).

Luminescent effects have been studied from calcite single crystals deformed dry at room temperature under a constant confining pressure of 2750 bars at a strain rate of 1 percent per minute (Handin et al., 1955; Lewis et al., 1956). The crystals exposed to 17 megaroentgens of gamma radiation and then deformed with the greatest principal stress paralleling the $\bar{c}$ -axis, resulting in translation gliding on $r\{10\bar{1}1\}$, changed in color from amber to blue and exhibited absorption maxima centering around 26000 cm^{-1} and 17000 cm^{-1} . With the least principal stress paralleling the $\bar{c}$ -axis (twin gliding on $e\{01\bar{1}2\}$) no color change resulted. Samples deformed by translation gliding show a new thermoluminescence peak, whereas the intensity ratio of the two highest-temperature peaks is altered after twin gliding.

Lewis (1956) considered it impossible at present to separate the effects of impurities from those of defect trapping centers for the 120°C thermoluminescence peak, but felt that the work on deformed materials favors a relation between the 240°C peak and the defect trapping centers.

Specific wavelengths of luminescent radiation have been attributed to particular impurity ions in carbonates (see Graf and Lamar, 1955), but the actual mechanisms rarely have been determined.

CARBONATE SEDIMENTS

EOLIAN SEDIMENTS

A sample of the dust carried over the Persian Gulf by prevailing winds from the northwest contained "83 percent calcite" (apparently the weight loss in HCl) (Emery, 1956). This sample is exceptional, however, for the maximum recorded carbonate contents in loess appear to be between 40 and 45 percent (Lamar and Willman, 1934; Leighton and Willman, 1950; Fisk, 1951; Swineford and Frye, 1955).

Newell and Boyd (1955) described a very coarse, eolian lag concentrate from the Ica Desert of Peru that locally consists of fragments of Eocene mollusks derived from nearby outcrops, the finer fractions having been winnowed out by the wind. Shell dunes on the Sonoran shore (Ives, 1959) have been similarly produced from recently elevated bottom marls. A section of foreset beds in one of the dunes of the Great Salt Lake Desert, Utah, consists of alternating 1-inch layers of granule-sized algal fragments and thick layers of gypsum arenite (Jones, 1953). Repeated intervals of maximum wind velocity are indicated.

SOILS

A few rudimentary soils (included here for convenience) are known, in areas underlain by limestones, that still contain at least 50 percent carbonates. Analyses of the Hikutavake rocky silt loam from Niue Island in the South Pacific (Schofield, 1959) and its parent limestone are given as analyses 11 and 12 (see Part IV). Incipient soils in the northern Marshall Islands are calcareous sands containing as much as 32 percent organic matter (Fosberg, 1954). Yaalon (1954) mentioned mountain marl soils from the Galilean Hills of Israel that contain more than 50 percent carbonates and are very low in clay minerals. The Galilean soils are really only physically disintegrated, friable limestone. The Lisan marl soils of the upper Jordan Valley are fairly deep and contain 20 to 50 percent carbonates.

GLACIAL DEPOSITS

Carbonate tills are formed when continental glaciers traverse areas of carbonate bedrock and subsequently deposit their loads of carbonate sediment before it has been unduly diluted by fragments of noncarbonate rock. Dreimanis (1957) stated that glacial drift in Ontario contains as much as 95 percent carbonate in places. The carbonate content of several glacially derived materials from Ontario, at least two of which would appear to have been redistributed by water after glacial deposition, are given below in table 1. Lamar and Willman (1934) listed three tills from Illinois that contain 22.41, 25.81, and 35.4 percent CO_2 . Analyses of the Mankato till in Manitoba (Ehrlich and Rice, 1955) showed up to 65 percent CaCO_3 , and a sample of till from the Iowan drift sheet in southwestern Minnesota lost 50.2 percent weight on treatment with cold dilute HCl (Kruger, 1937).

Most pebble counts of tills reported in the literature that show a majority of carbonate pebbles have not been included in table 1 because one cannot be certain that other particle-size ranges have the same carbonate content. The calcareous content of Wisconsinan till in the Upper Whitewater Basin, Indiana-Ohio, for instance, drops from 70 percent in coarse sand and gravel to 25 percent in medium and fine sand, 40 percent in very fine sand, 30 percent in silt, and 15 percent in

Table 1. - Carbonate Content of Some Glacial Till in Canada and the United States

A - from Dreimanis (1957)	Total percent carbonates	Probable age of deposit (years)	Remarks	
(Glacial) Lake Algonquin beach, Orilla, Ontario	70	8,000-9,000	No dolomite pebbles	
Pebbly gravel, Fanshawe, Ontario	80	14,000	More limestone than dolomite pebbles	
(Glacial) Lake Warren beach barrier, Union, Ontario	50	9,600-12,000	More limestone than dolomite pebbles	
Mitchell moraine, Elginsfield, Ontario, with 90% carbonate pebbles	65		More limestone than dolomite pebbles	

B - from Anderson (1957)	Sand grains (%)		Pebbles (%)	
	Limestone	Dolomite	Limestone	Dolomite
Erie lobe (Wisconsinan Stage), northeast Indiana	36	17	50	13
Erie lobe (Wisconsinan Stage), northeast Indiana	23	28	30	41
Lake Michigan lobe (Wisconsinan Stage), Rockdale moraine, northeast Illinois	4	63	2	75
Green Bay lobe (Wisconsinan Stage), Valders moraine, southeast Wisconsin	1	60	0	93
Green Bay lobe (Wisconsinan Stage), Rush Lake moraine, southeast Wisconsin	0	81	0	90

clay (Thorp et al., 1957). Several of Anderson's (1957) samples, for which particle counts are given for both sand and pebbles, are shown in table 1. The lesser carbonate content of the sand sizes compared with that of the pebbles in Anderson's study results, at least in part, from a concentration of the Precambrian quartz and feldspar grains in the sand-size range. The Trenton and Black River Limestones of Ordovician age under Lake Erie furnished the limestone particles in the Erie lobe samples. The Niagaran age (Silurian) dolomite and the dolomites in the Prairie du Chien Group and the Galena Formation of Ordovician age were the sources of the dolomite particles in the Lake Michigan lobe and Green Bay lobe samples.

STREAM DEPOSITS

Stow (1930) described pea- to egg-sized, layered CaCO_3 concretions, of uncertain derivation but apparently of inorganic origin, which occur near Lexington, Virginia, in streams draining limestone terrain but not in those draining sandstone or Precambrian crystallines.

Stream-borne carbonate particles are reduced in size and number because they are susceptible both to abrasion and breakage and to solution. Thus Plumley (1948) found that the percentage of limestone plus sandstone pebbles 16 to 32 mm in size was reduced 90 percent in a distance of 30 miles along Rapid Creek, South Dakota.

Along the Virginia and Maryland streams examined by Hack (1957), coarse limestone boulders enter the stream from undercut cliffy slopes and remain near their source as a lag concentrate. Breakage and abrasion reduce the boulders, and pebbles in the bedload persist for five miles or less downstream, depending on the physical properties of the limestone. Thus there is only a very short interval from a given outcrop in which fluvial carbonate sediment can persist. During the summer calcareous tufa forms on the stream bed at riffles in Middle River, so at that time solution does not appear to be even a minor factor. Limestone pebbles persist, however, for much greater distances in the Colorado River of Texas than in the streams mentioned above. Sneed and Folk (1958) found that 68 percent of the pebbles at the farthest downstream limestone outcrop were limestone, 30 miles from the outcrop 50 percent were limestone, 54 miles from the outcrop, 40 percent, 176 miles, 3 percent.

At points sufficiently close to sources of abundant carbonate detritus, such as carbonate outcrops in arid regions or areas of high relief, stream deposits may be actual carbonate sediments. One probable example is a portion of the Colorado River in Texas, described by Sidwell and Cole (1937), along which the pebbles and boulders are primarily limestone. Udden (1914) described gravels of Pleistocene age along the lower Rio Grande River in Texas that consist of white limestone derived from the Pennsylvanian outcrops found in the westernmost part of the state. He described similar gravels now being formed in the wide channels of Tequesquite and other creeks that are tributaries to rivers draining the Edwards Plateau. When flooded, these creeks roll broad sheets of limestone gravel several hundred feet wide. The Molasse beds of southern Germany contain from 25 to as much as 50 percent detrital dolomite-rock grains, which become smaller in size away from the Alps, and some 25 percent calcite (Hans Füchtbauer, personal communication). The Alpine fans contain up to 80 percent limestone and dolomite, much of it in large, only slightly degraded blocks.

By the time rivers that have attained maturity or old age in their lower courses reach the ocean, however, they are transporting practically no carbonate. A composite of analyses of Mississippi River silt at the Mississippi delta shows only 1.40 percent CO_2 (Clarke, 1924). The fluvial solids contributed to marine carbonate sediments are therefore almost entirely noncarbonate.

FRESHWATER LAKE SEDIMENTS

The mud in the deep central part of Lake Zurich consists of alternate laminae rich in microgranular carbonates and in organic matter. Nipkow (1927) noted that each summer his plankton nets were clogged by particles of CaCO_3 precipitated from the surface waters of the lake. He correlated variations in the diatom size distribution, mud content, and thickness of the top layers of the cores with shore slumps he had observed and with diatom size distributions obtained from eight years of surface collections. The laminae are therefore nonglacial varves.

Glacio-lacustrine sediments in northeastern Wisconsin contain appreciable dolomite rock flour believed by Thwaites (1943) to have been mechanically transported from the parent till. Ellsworth and Wilgus (1930) found as much as 25 percent of this material in summer layers and as much as 50 percent in winter layers.

Soft, argillaceous, CaCO_3 -rich deposits (marls) that locally are rich in shells occur as postglacial freshwater deposits from western New York through the Middle West in many swamps and lake basins. In their study, Blatchley and Ashley (1901) observed that these deposits are found only in those Indiana lakes occurring in drift areas (see also Stout, 1940), and that the thickest deposits

are in areas where the drift is thickest. Similarly, Thiel (1930, 1933) concluded that the marls are best developed where the basins are surrounded by high morainic hills of coarse-textured outwash gravel sufficiently porous to be effectively leached of carbonate by ground water. This is so even though the clayey-textured moraines have a higher percentage of CaCO_3 than the sandy-textured ones, and even though the ground water in the former contains an average of 138 ppm CaCO_3 compared with an average of 59 ppm in the latter.

Thiel noted that in chains of deep lakes marl may occur in any of them, but in chains of shallow lakes the greatest amount of marl is in lakes toward the head of the chain. Such lakes gradually become filled with marl until vegetation is able to gain a foothold and a swamp is formed (Smith, 1916; Davis, 1901). Deposits of marl underlying peat deposits in Ohio may be several feet thick and may cover several square miles (Dachnowski, 1912). Teichmüller (1954) described a Swabian peat deposit located in a closed basin between an older (Riss), carbonate-poor moraine and a younger (Würm), carbonate-rich one; the freshwater limestones intercalated in the peat occur only in the part of the basin close to the Würm moraine.

Lundqvist (1936) showed on a map of Sweden the lakes in which calcareous sediments occur, and Thunmark (1937) indicated that in southern Sweden such calcareous lacustrine deposits coincide either with areas rich in outcrops of carbonate rock or with areas immediately south of the outcrops in which glacial deposits are rich in carbonate. Marl deposits in British Columbia commonly are found in lakes of the interior where the climate is drier, and in most cases such deposits are near limestone outcrop areas (Mathews and McCammon, 1957).

A marked decalcification of the water of the River Susaa is observed after it has passed through two Danish lakes, Tystrop Sø and Bavelse Sø, which have sediments containing as much as 75 percent calcium carbonate (Berg, 1943; Hansen, 1959).

The "marl islands" that rise almost to the surface of Tippecanoe and Winona Lakes in Indiana lie atop knobs or swells of the original bottom (Wilson, 1936, 1938). The thickest marl deposits are in the deep parts of the lakes and the thinnest are on steep slopes and in the zone of wave action near shore. A comparison of sediment volumes and water areas in various parts of Tippecanoe Lake shows that erosion of the sediments forming in the shallows is greater at the leeward end of the lake where the wave action is more vigorous than at the other end of the lake.

In the lakes that they studied, Blatchley and Ashley (1901) found a correlation in thickness of marl deposits with nearness to spring outlets in the lakes, a relation they attributed to CO_2 loss from the spring water as it warmed. In central Pope County, Minnesota, where an impervious till seals porous sands and gravels containing water under hydrostatic pressure, marl deposition is extensive around springs at points where lake basins have cut below the till (Thiel, 1933).

More often, however, marl deposition is limited to the shallow waters of the lakes, as was the case for the lakes that Davis (1903) examined. The fine-grained CaCO_3 deposit in Lake Neuchâtel is also thickest in the shallowest waters (Portner, 1951). Kindle (1927, 1929) found lacustrine marls limited to relatively small areas that were shallow and protected from wave action in lakes where altitude and latitude did not keep the temperature of the epilimnion zone too low for the development of *Chara*, *Potamogeton*, and other plants of widely different types that extract CO_2 . Higher water temperatures in the shallows aid deposition of CaCO_3 by decreasing both the solubility of CaCO_3 and of CO_2 . The waters of the cold, deep zone are rich in CO_2 and would dissolve carbonate.

Several species of the Charae, nonmarine plants known since early Devonian times, contribute to freshwater limestones and marls by secreting CaCO_3 from the vegetative cells and within the spiral enveloping cells of the oogonia (Peck, 1957). Davis (1901) found an appreciable amount of calcium succinate in the cell sap of *Chara*. The CaCO_3 deposited in the vegetative parts frequently, but not always, disintegrates when the plant dies, and it is the small spiral calcified parts of the oogonia that are recognized in nonmarine limestones that often contain few other fossils.

The numerous white, calcareous cakes from 1 to 5 cm in diameter, described by Clarke (1900) from the north shore and nearby bottom of Canandaigua Lake, New York, are made up of concentric layers of travertine, but a soft, spongy, organic residuum of the same volume as the original cake remains after treatment with dilute acid. Roddy (1915) and Howe (1932) described similar cakes from streams. Examination of residues and thin sections reveals a mixture of minute plants — diatoms, unicellular and filamentous Myxophyceae (Cyanophyta), and unicellular Chlorophyceae. The fine-grained, spongy, arborescent, carbonate masses described by Bradley (1929a) from the shores of Green Lake, New York, were attributed by Rezak (1957) to CaCO_3 precipitation as a result of algal photosynthesis. Mawson, cited in Twenhofel (1932, p. 312), has described "algal biscuits" from shallow interdunal lakes underlain by limestone in South Australia.

The marl deposits in Littlefield Lake, Isabella County, Michigan, as described by Davis (1900, 1901) were 25 to 30 feet thick near shore but thinned markedly as the water deepened. The surface of the shallow bottom was covered with growing *Chara*, and the beaches and upper sediment layers consisted largely of brittle, fragile remains of *Chara* that broke into fragments at a touch, and pebbles that showed bluish green radiating lines of filamentous algae (*Zonotrichia*, *Schizothrix*) when broken open.

Marl deposits found in sheltered embayments and marginal areas of five lakes in the Knik Arm area of Alaska contain from 12 to 77 percent CaCO_3 , depending on the amount of clastic material and organic matter admixed (Moxham and Eckhart, 1956). The marl completely fills some embayments and has been covered by a layer of muskeg. *Chara* and possibly some blue-green algae are responsible for the deposit in Edlund Lake.

The freshwater lake sediments in Wisconsin contain (Twenhofel and McKelvey, 1941) proteins, cellulose, lignin, fats, waxes, gums, and resins contributed principally by water plants, together with terrigenous detritus, siliceous diatom tests, shells of freshwater gastropods, and microscopic CaCO_3 crystals. The gastropods are a significant contribution in only one of the lakes these authors examined. The black sludge in Lake Monona beyond a belt of muddy shore sands contains 8 to 48 percent CaCO_3 (typically 38 percent) and overlies firm, light colored sediments containing from 51 to 83 percent CaCO_3 (typically 65 percent), 0.47 to 2 percent MgO, 0.5 to 4.1 percent Al_2O_3 , 0.5 to 1.8 percent Fe as Fe_2O_3 , and organic matter, clay, and silica present as detrital quartz grains and diatom tests. This sediment would correspond to a generally fine-grained, siliceous, slightly argillaceous limestone.

The comparable material in the deeper parts of thermally stratified Lake Mendota (Twenhofel, 1933) contains 60 to 80 percent CaCO_3 , 13 to 25 percent SiO_2 , 0.5 to 0.8 percent Fe as Fe_2O_3 , 0.3 to 3.3 percent Al_2O_3 , and 1.3 to 5.6 percent MgO. Murray (1956) reported an average of 32.2 percent carbonate in the Lake Mendota sludge, 62.7 percent in the underlying marl, and 54 percent in the gray to dark gray marl that it appears is still being deposited in Lake Wingra.

A blue plastic marl containing an average of 77 percent carbonate and a pink clay that contains clastic dolomite pebbles and may have up to 43.6 percent carbonate also are found in Lake Mendota. The percentage of P_2O_5 in the Lake Mendota cores, without regard for lithologic type of sediment, ranges from 0.168 to 0.275 percent, averaging 0.20 percent for 15 determinations. Twenhofel stated that some 30 feet of marl has accumulated in hard-water Lake Mendota since the departure of the glaciers, in contrast to as little as 3 feet in soft-water lakes.

Murray (1956) found a sharp interface between the sludge and underlying marl in Lake Mendota, with no evidence of diagenetic chemical changes. The total organic content is only slightly different on the two sides of the interface — 12.4 versus 13.2 percent — but the sludge contains more clastic material than does the marl. The black color in the marl results from authigenic ferrous sulfide, whose presence is inferred from the presence of $<1\mu$ grains of a metallic mineral that has properties consistent with those of pyrite, and from rates of loss of sulfur and ferrous iron, incurred when the sludge is allowed to stand, essentially in the ratio FeS_2 . The available supply of lime in the glacial drift apparently has diminished with continued leaching and with the formation of a sediment seal between lake water and ground water, a situation also described by Groschopf (1936) for the Grosser Plöner See in East Holstein. The decrease in available lime, however, occurs gradually, and the sharp marl-to-sludge transition is attributed to an increase in the supply of clastics and organic material from cultivation and a consequent decrease in the oxygen available to the sediments.

Some of these marls are jelly-like and have high water contents. A sample from Douglas Lake, Sheboygan County, Michigan, lost 47.99 percent in weight on drying (Wilson, 1945). Samples from Cheam Lake, British Columbia, even after partial drying in bins, lost from 50.6 to 55.0 percent water at $105^\circ C$ (Mathews and McCammon, 1957).

The sediments around a small island bird rookery in Cuthbert Lake, Florida, are a mixture of peat, marl shell fragments, fragments of Miami Limestone from the bedrock, and concretion-like particles, principally fluorapatite. The P_2O_5 content of 11 samples collected at various points around the island ranged from 0.48 to 7.92 percent (average 4.10 percent), whereas four marl samples from near the edge of the lake had only a trace to 0.18 percent P_2O_5 (Lund, 1957). Although the bird colony seems to be playing a part in phosphate accumulation in this lake, Lund describes several other Florida localities at which calcareous sediments near rookeries contain only a trace to at most 0.41 percent P_2O_5 .

The stagnant bottom waters of deep, narrow Lake Tokke (Strøm, 1957) are exceptional because all the sulfate apparently has gone to form H_2S and because the iron bicarbonate content is high. This water is compared below with sea water recomputed to the same chloride content. A coring program was said in 1957 to be under way, and it is conceivable that this lake may prove to be the first significant site of present-day siderite deposition to be described.

	A	B		A	B		A	B
Cl^-	9190	9190	Na^+	5145	5000	B	13	no analysis
Br^-	47	no analysis	K^+	188	0	Fe	0	393
$SO_4^{=}$	1283	0	Mg^{++}	616	781	NH_3	0	145
HCO_3^-	69	3800	Ca^{++}	198	245			

A - Sea water with 9190 mg Cl ions per liter.

B - Lake Tokke water (Norway), 144 mm depth, collected October 7, 1951.

SALINE LAKE SEDIMENTS

Krivan (1954) described a series of shallow basins that drop some 25 meters in elevation in 35 kilometers distance between the Danube and Theiss Rivers in Hungary. Holocene-age sediments in these basins include freshwater, CaCO_3 -rich materials containing large numbers of water snails (*Planorbis* sp.), as well as dolomite-rich sediments identified by X-ray diffraction. The carbonate particles are all <0.002 mm in diameter, whereas detrital quartz has size maxima both in this size range and in that around 0.1 mm.

Krivan claimed a lateral and vertical succession within individual basins from freshwater limestone to dolomite to carbonate deposits containing up to 0.4 percent Na_2O . The over-all content of Mg and Na is said to increase with progression along the series of basins. The Ca and Mg presumably were derived from leaching of nearby calcareous loess and sand dunes. Springtime high waters are believed to have filled the basins and perhaps dissolved some material and transported some to lower basins until evaporation lowered the water level to where individual basins regained their identity.

Remnants of Glacial Lake Bonneville

Great Salt Lake has a salinity of from four to ten times that of the ocean, depending upon seasonal volume, but about the same ionic balance (Eardley, 1938), and carbonate deposition has been the dominant chemical process for some time. Oolite formation around detrital minerals and the fecal pellets of the brine shrimp *Artemia gracilis* is prominent along shore lines that face the open lake and receive unimpeded waves. Algal masses, particularly of *Aphanothece packardii*, have formed in shallow water and contain much entrapped fragmental material. Clayey lime ooze found in the middle of the lake between islands becomes calcareous silt between the islands and shore because of the addition of terrigenous material.

The absence of localized CaCO_3 precipitation around river mouths and its rather uniform deposition over the entire western part of the lake indicate that CaCO_3 precipitation occurs during the yearly lowering of lake level by evaporation after the heavy spring influx of river water has had a chance to mix with the lake waters. Eardley estimated that one third of the lake sediments are pelletized and noted that analysis of a pellet sand showed some 77 percent carbonate. This compares with his other estimated average carbonate percentages: 21 percent for all clays, 70 percent for algal deposits, 84 percent for oolites. These three sediments cover the bottom areas about in the proportion 70:10:20.

Graf et al. (1959) have described a thin zone of nearly pure, fossil-free, unconsolidated dolomite occurring about a foot below the surface of the Lake Bonneville sediments in the Great Salt Lake Desert. The C^{14} date of 11,150 years for the dolomite, obtained assuming the present $\text{C}^{14}/\text{C}^{12}$ ratio in Pyramid Lake as control (W. S. Broecker, personal communication), correlates with a widely observed onset of a drier climate during the Pleistocene (Broecker et al., 1958; Flint and Gale, 1958). Closer to shore is encountered an assemblage of aragonite and a magnesite with a significantly enlarged unit cell, believed to result from hydration.

Remnants of Glacial Lake Lahontan

Masses of tufa of three different textural types — lithoid, thinolitic, and dendritic — are found throughout the area occupied by former Lake Lahontan. The thinolitic tufa is made up of irregularly oriented, tetragonal-appearing pyramids of

calcite, which J. D. Dana (quoted in Russell, 1889a) believed to be leached and replaced crystals originally precipitated as another compound, perhaps Na-Ca carbonate, and which Jones (1925) believed from goniometric measurements to be pseudomorphous after aragonite.

Radbruch (1957) found isolated crystals with their long axes pointed toward the surface in fresh muds recently exposed by a drop in water level in Pyramid Lake. The crystals become more skeletal downward in the mud and away from the harder zones in nearby thinolite tufa domes. They apparently form only in fine-grained calcareous mud and are believed by Radbruch to be forming at present.

Dunn (1953) showed that tufa in present-day Mono Lake, another remnant of Lake Lahontan, forms from the mixing of lake water with cold spring water that enters the lake with a high calcium bicarbonate content acquired in passing through nearby areas of marble. When the waters mix, appreciable precipitation occurs, as shown by the formation of tufa towers at points where springs emerge. The insoluble residue of the tufa contains opal, presumably formed in the lake, and quartz and other detrital minerals derived from nearby metamorphic and batholithic rocks. The argillaceous sediments of the floor of Pyramid Lake are also highly calcareous; Radbruch (1957) noted that a sample from the west side of Pyramid Lake lost 60.4 percent of its weight on treatment with dilute HCl.

Caspian Sea

The shallow western and deep central parts of the Caspian Sea are largely covered by fluvial sediments and are low in carbonates, which in 1913 and 1914 were found to make up only 15.2 and 18.4 percent, respectively, of the suspended load in the Kura and Arax Rivers. However, practically no rivers discharge along the whole eastern part, which is bordered by a semiarid region and has a high rate of evaporation, and there is heavy CaCO_3 precipitation involving oolites, abundant deposits of shells, and fine-grained carbonates. The outcrops of the eastern near-Caspian region are high in carbonates, so that eolian material from that area contains abundant carbonate (Bruevich and Vinogradova, 1946). Alternating dark and light laminae like those of the Black Sea are found at depths below 800 meters, where a euxinic, H_2S -bearing environment is first encountered.

The carbonate fractions of the white silts in hypersaline (21 to 22 percent salinity) Karabogaz Bay of the Caspian Sea are usually less than 50 percent of the sediment but may show far more MgCO_3 than CaCO_3 in the analyses; for example, 1.66 percent CaCO_3 and 11.36 percent MgCO_3 at station 4, 1.33 percent CaCO_3 and 10.61 percent MgCO_3 at station 22, 17.54 percent CaCO_3 and 16.17 percent MgCO_3 at station 39 (Strakhov, 1947). L. V. Selivanov, quoted by Strakhov, held Karabogaz Bay sediment in its brine for four years and then obtained on analysis, after correcting for brine still contained in the sample, MgCO_3 , 53.12 percent; CaCO_3 , 18.68 percent; CaSO_4 , 5.82 percent; insoluble residue, 14.86 percent; $\text{MgCO}_3/\text{CaCO}_3 = 2.85$. P. A. K'olodub, quoted by Strakhov, obtained an even higher $\text{MgCO}_3/\text{CaCO}_3$ ratio, 4.96, for another sample.

These MgCO_3 -rich sediments form a surface layer only 0 to 12 cm thick, below which there are calcite-rich sediments. Records of explorers in the mid-1700's and very early 1800's show that fish were then abundant in the bay which had not yet become hypersaline.

Aral Sea

The waters of the Aral Sea have a typical salinity of 9‰ or 10‰ and an average pH of 8.3, although these values vary with geographic location, depth, and season. There are banks of molluscan, ostracodal, and foraminiferal shells near shore and on part of a central rise, but the plankton are generally unimportant as lime secreters. Oolites are forming at several places to the northwest of the island of Vozrozhdenia, where colder waters from the western depths flow across shallows that are warmed clear to the bottom. The minute CaCO_3 needles found in the shallow water of the Bogamsky Bank and in the slowly accumulated deep-water deposits have a shape different from that of the detrital particles brought into the delta areas by the rivers, and they are believed to be chemical precipitates. Sediments containing more than 50 percent carbonate are found in the deepest parts of the two basins in the lake where the terrigenous contribution is small and there has perhaps been a hydrodynamic concentration of precipitated carbonate from a wider area. Carbonate concentrations as high as 68 percent have been observed.

Sediments in the northern basin show annual pairs of light and dark laminae varying in content of organic matter (Raupach, 1952). In the western and central basins these laminae differ in grain size and texture but not in color. Sharply varying salinities in the latter two basins are believed to limit plankton to euryhaline types and thus to decrease the amount of organic matter in the varves. The Amu Daria (River) in summer carries 16.6 percent CaCO_3 in its suspended load, the Syr Daria 21 percent. The latter typically carries 2.9 million tons a year of suspended CaCO_3 , 1.7 million tons dissolved. The amount of dissolved CaCO_3 transported increases during the winter months and exceeds the suspended CaCO_3 .

The limy sands contain an average of 0.29 percent organic carbon and 0.41 percent Fe, computed on the basis of natural sediment; the marls have 0.94 percent and 2.7 percent (Brodskaya, 1949, 1952; Strakhov, 1951).

Alekhin and Moricheva (1955) estimated that salinity in the Aral Sea will triple in the next fifty years because of the increasing use of water from the Amu Daria and Syr Daria for irrigation.

Lake Balkhash

The gradual change in composition of the water in Lake Balkhash in successive pools from west to east is given in tables 2 and 3 (Sapozhnikov, 1951). The easternmost pools have higher temperature, pH, and alkalinity, and the bottom muds contain more organic material in the colloid fraction, more iron, more Mg, and more F and B than those in the pools to the west (Zalmanson, 1951) (analysis 20, see Part IV). The presence of magnesite, in addition to dolomite, in these muds is claimed from the analyses. Total carbonate in the microgranular sediment of the easternmost pool reaches 70 percent but the areas covered by sediments with more than 50 percent carbonates decrease in successive pools toward the west. The percentage of dolomite present, computed from chemical analyses, is important in only the two eastern pools, Lepsinskij and Biurliuj-Tupinskij. This percentage fluctuates in cores, showing no obvious relation to depth. Thus, in the depth range from 5 to 10 cm in a core from the center of the Biurliuj-Tupinskij pool, the amount of dolomite computed from chemical analysis as percentage of total carbonates was 57.4; in the range 31 to 33 cm, 5.6 percent; from 45 to 47 cm, negligible; from 59 to 61 cm, negligible; from 66 to 68 cm, 93.1 percent. Some of the low-Mg zones are 0.5 to 1.5 mm interlayers consisting almost entirely of the shells of diatoms and ostracodes.

Table 2. - The pH and Content of Principal Ions in the Several Pools of Lake Balkhash, from West to East (Sapozhnikov, 1951)

	In milligrams per liter				pH
	CO ₃ ⁼	HCO ₃ ⁻	Ca ⁺⁺	Mg ⁺⁺	
Western pool, estuary of River Ill	22.8	270.9	55.7	77.0	8.2
Western pool, southern part	20.5	280.5	37.4	74.0	8.3
Western pool, middle part	22.2	292.1	37.4	81.9	8.4
Western pool, northern part	25.2	334.3	42.2	99.0	8.4
Middle pool, western part	48.9	443.8	25.7	164.	9.0
Lepsinskij pool	86.6	628.4	17.0	240.	9.15
Biurliuj-Tupinskij pool	102.8	683.8	15.1	285.	9.2
Biurliuj-Tupinskij pool	122.1	662.8	14.0	289.	9.15

Table 3. - Chlorine Coefficients of Ions in the Waters Described in Table 2 (Sapozhnikov, 1951)

	CO ₃ ⁼	HCO ₃ ⁻	SO ₄ ⁼	Ca ⁺⁺	Mg ⁺⁺	K ⁺ + Na ⁺
Western pool, estuary of River Ill	9.62	114.30	156.12	23.50	32.49	106.33
Western pool, southern part	9.00	123.02	155.26	16.40	32.46	117.11
Western pool, middle part	8.54	112.35	151.92	14.38	31.50	115.38
Western pool, northern part	7.95	105.46	153.31	13.31	31.23	114.51
Middle pool, western part	8.52	77.32	155.57	4.48	28.57	120.91
Lepsinskij pool	9.08	65.87	147.80	1.78	25.16	123.06
Biurliuj-Tupinskij pool	9.51	63.26	150.60	1.40	26.36	121.65
Biurliuj-Tupinskij pool	11.03	59.87	152.21	1.26	26.11	123.13

Lake El'ton

Large, viscous, gray lumps of material found in highly saline Lake El'ton have, after they have been washed to remove Cl⁻ and SO₄⁼, the composition shown by analysis 21 (see Part IV). Vital (1951) considered the analysis indicated that most of the sample is made up of basic salts of magnesium carbonate; no explanation was offered for the high percentage of Mn.

Ephemeral Australian Lakes

The best-documented case thus far for the present-day formation of dolomite is that described from South Australia by Alderman and Skinner (1957). Precipitation of dolomite is taking place in the Coorong, a long narrow arm of the sea, and in Kingston Lake and Lake Hawdon North, interdunal lakes with relatively impervious floors in an area where most drainage is underground through Pleistocene and Recent dune rocks. The water has essentially the same ionic balance as sea water, but it is only from one-tenth to one-half as saline. The lakes dry up during the summer, but animal and plant life start up again after the winter rains, especially *Ruppia maritima* Linn., and reach a maximum during November and December. Values of pH as high as 9.2 have been observed in the vicinity of plentiful masses of *Ruppia*, which are believed responsible through photosynthesis for raising the pH above the normal figures of 8.2 to 8.4. In the *Ruppia* areas the water is often turbid with fine, white carbonate sediment settling to the lake floor. X-ray dif-

fraction diagrams show that the material in suspension and the bottom material contain variable proportions of calcite with up to 22 percent magnesium carbonate substitution and dolomite with up to 6 percent excess CaCO_3 (Alderman, 1959). The carbonates all have a high Sr content, up to 1 percent, and fine-grained SrSO_4 has been identified in the samples (H. C. W. Skinner, personal communication). Analysis 18 (see Part IV) is that of a typical sediment sample containing some shells and some noncalcareous detrital material.

Bonython (1956) described a zone of dolomite sediment with the consistency of stiff white pipe clay that occurs at a depth of 11 to 12 feet below Lake Eyre North, South Australia, and contains numerous small pellets of lithified dolomite (analysis 19, Part IV).

BEACH DEPOSITS

Carbonate-rich beach deposits are widespread in the tropical zone of abundant marine organic carbonate production. They have been described, for example, on the east and northeast coasts of Puerto Rico (Guillou and Glass, 1957) and on the parts of the Mediterranean coast of Egypt not reached by lateral transport of Nile sediments (Hilmy, 1951). The carbonate content is reinforced in the former case by erosion of consolidated calcareous sand, in the latter apparently by eolian transport of limestone particles from outcrops of Cretaceous and Eocene age in the nearby Western Desert.

A progressive change in composition is shown by beach deposits along the southeastern Atlantic coast of the United States. The southward-flowing current there carries quartz, feldspar, and heavy minerals from the metamorphic and igneous rocks of the Piedmont. Although some North Carolina beaches are carbonate sediments (Tyler, 1934) containing as much as 93 percent CaCO_3 , consistently high CaCO_3 percentages are reached only in south Florida where there is a sharp decrease in detrital quartz, in particular, and a great increase in organic productivity of CaCO_3 (Martens, 1931).

Favorable hydrodynamic conditions may cause carbonate beach sediments to form locally in regions where such accumulation would otherwise be impossible. Protection by Cedros Island and lack of a more or less continuous contribution of sediment from longshore drift has resulted in the accumulation of small beaches of locally derived shell sand on the southeast side of the island, in Sebastian Viscaïno Bay, Baja California (Emery et al., 1957).

Carbonate sediments can accumulate locally on cool-water beaches at relatively high latitudes if the rate of accumulation of inorganic detritus is low, the local cool-water, biogenic carbonate is concentrated from a larger area, and the beach is not subject to severe wave action capable of dispersing the accumulated carbonate sediment. At John O'Groats, Scotland, the beach sand (analysis 25, in Part IV) consists largely of shells, with some quartz grains, biogenic detritus, and a few fragments of sandstone (Raymond and Hutchins, 1932). Locally complex tidal currents push material from an extensive bottom area onto the beach. A low bluff of lithologically similar material at the rear of the beach, analyzed as 95 percent CaCO_3 and containing peat, also contributes to the beach.

Storm waves grind up and sweep shells from a large area into Cranberry Harbor, Maine, from which weaker local waves transport the fragments onto a beach that is formed of 67 percent CaCO_3 (Raymond and Stetson, 1932) and some fragments of local igneous and metamorphic rocks and minerals. The beach at Dog's Bay, Ireland, is made up chiefly of foraminiferal shells as a result of a fortunate combination of directions of local currents and the North Atlantic drift.

Some beaches in the Mingan Islands, Gulf of St. Lawrence, are made up of dolomite sands derived from erosion of the dolomite outcropping on the island. Similarly, many sands on the beaches of Gotland and Anticosti Island are more than 90 percent limestone fragments (Twenhofel, 1932).

REEFS

Lowenstam (1950) defined a true reef as "the product of the actively building and sediment-binding biotic constituents which, because of their potential wave resistance, have the ability to erect rigid, wave-resistant topographic structures." Reefs are thus to be contrasted with shell mounds and with those accumulations of skeletal debris formed by biotic communities which were only moderately successful in erecting wave-resistant structures. Groups of plant and animal contributors change with geologic time (Forman and Schlanger, 1957; Cloud, 1952). Calcareous sponges, hydrocorallines, stromatolites, and bryozoa, corresponding to corals and algae today, were the framework-builders for the Capitan Reef of Permian age (Adams and Frenzel, 1950; Newell, 1955).

The faunal and floral assemblages of the characteristic areal zones of reef complexes are essentially the same for a given geologic period, and the local geologic setting is unimportant if ecologic conditions are met (Forman and Schlanger, 1957). Reefs grow on any sort of foundation that projects into shallow water — the examples that have been cited include wave-cut platforms and fluvial delta sediments (Ladd, 1950), the flanks of an intermittently active volcano and a ridge of folded volcanics at Guam, piercement salt dome structures and a shallow shelf in southern Louisiana (Forman and Schlanger, 1957).

Vigorous growth of present-day reefs generally is limited to the area between 30° north and 30° south latitude, which also largely includes the farthest north and farthest south annual extensions of the 70° isotherms. To interfere with reef development in this latitude range, a river must have considerable sediment-carrying capacity. Coral reefs and calcareous sands of organic origin accumulate even in bays of the tropical islands of the Pacific, such as Pago Pago Harbor (Bramlette, 1926). Even though there is strong topographic relief and heavy rainfall, the island streams drain such small areas that no large amount of clastic material is contributed to the bays beyond the immediate mouths of the streams.

At Murray Island, Australia, the beach has much basaltic material, but 200 feet seaward from shore the content of ($\text{SiO}_2 + \text{Fe} + \text{Al}_2\text{O}_3$) is only 0.63 percent (Vaughan, 1918). A similar general absence of igneous rock fragments occurs in the near-shore coral lagoon sediments from Raiatea, Society Islands (Stark and Dapples, 1941); the beach and barrier reef both protect the cliff from erosion.

The algal need of light for photosynthesis places a limitation upon the depth at which present-day reefs form. Cloud (1952) estimated that calcareous algae of any geologic age must have lived at less than 50, and probably less than 25, fathoms. Both light and temperature affect the reef-building corals (see Vaughan, 1919). The reef corals at Bikini diminish rapidly to a depth of about 45 fathoms, and only one or two species are found at 85 fathoms (Ladd et al., 1950). Emery et al. (1954) noted that some of the reef-type algae at Bikini, together with large foraminifers, appear able to construct reef foundations several hundred feet below the lower limit of corals, which contribute to the structure only when its growing surface reaches shallower depths. Ladd and Hoffmeister (1945) described elevated coral reefs resting on bedded algal-foraminiferal rocks on the main islands at Fiji. Relatively clear water of near normal salinity, together with water circulation adequate to furnish a food supply, also are essential for reef building (Ladd, 1950).

These delicate environmental requirements of reefs render them sensitive to both changes in sea level and foundation rises or falls. Eniwetok is a thick cap of mostly soft or weakly consolidated limestone, of Quaternary through Eocene age, that rests on the summit of a volcano rising two miles above the sea floor (Ladd et al., 1953). The Miocene and younger beds are made up entirely of shallow-water organisms. The aragonite of corals and mollusks has been dissolved away in some zones, indicating a period of elevation above sea level, but is preserved in others, including the 810 to 880 foot depth interval. The absence of cementation in the upper few hundred feet at Eniwetok indicates that the present rims grew up after the last low (glacial) sea level, at a rate some ten times that for the Tertiary. Gaps in the reefs indicate they could not keep up with this sea level rise and were drowned (Kuenen, 1954).

The distribution and orientation of patch reefs in the relatively deep lagoon at Kapingamaringi Atoll seem to be directly related to the strong currents and waves that maintain good circulation (McKee, 1958). The lagoonal sediments at successive depth zones are clearly differentiated as a result of beach sorting and of the particular organisms dominating the submarine zones. Foraminiferal deposits of *Amphistegina madagascarensis* and lesser numbers of *Marginopora vertebralis* are succeeded in progressively deeper water by comminuted shell sand, coral rubble, calcareous green algal detritus (*Halimeda*), a zone of *Amphistegina lessonli* remains, and finally a CaCO_3 ooze containing about 10 percent slimy organic residue. X-ray diffraction shows that all coral limestones from the islands at Kapingamaringi contain more than 90 percent aragonite. The calcareous ooze at the lagoon center is aragonite surrounded by a belt of calcitic remains of *A. lessonli*, indicating that the ooze is not a hydraulic concentration of fines from upslope.

The organic carbon content of the sediments in Bikini lagoon (Emery et al., 1954) ranges from 0.18 percent for beach deposits to 0.62 percent (average 0.46 percent) for 11 samples other than beach deposits. Analysis 26 (see Part IV) is of this material.

Oyster reefs form in brackish water and often constitute local lenses of carbonate enclosed in carbonate-poor detrital sediments. Oysters grow on sandy bottom in San Francisco Bay (Loudenback, 1920), on the sediments of Chesapeake Bay, which are dominated by quartz (Ryan, 1953), and on the quartz-rich bottom muds of Mississippi Sound, which contain some iron sulfide and a little organic matter (Priddy, 1955). Oyster reefs are present in central San Antonio Bay and have been encountered in borings on the central Texas coast (Shepard, 1956).

The ahermatypic corals are a striking exception to what has been said about temperature and depth requirements, for they occur at all depths down to 20,000 feet and in temperatures as low as -1.1°C (Teichert, 1958). Rich banks and patches lie at the edge of the continental shelf off western Europe and at entrances to large Norwegian fjords, both places where upwelling Atlantic water supplies nutrients. Teichert also mentioned extensive calcareous algal banks extending from the shallow, cool waters of the temperate zone to well within the Arctic Circle.

CONTINENTAL SHELF OFF EASTERN NORTH AMERICA

Sediments at depths of about 100 fathoms along the outer edge of the continental shelf from Cape Cod to Maryland are in many places half foraminiferal shells, principally *Globigerina* (Alexander, 1934). They also contain shells of some benthonic forms, considerable organic matter, and green glauconitic mud. Tiny spheroids of iron sulfide are found, invariably enclosed in shells of foraminifera where decaying organic matter produced intense local reducing conditions.

Longshore currents carry fine-grained quartz sand southward from the coast of South Carolina and Georgia along the inner part of the continental shelf to the middle of east Florida (Dunbar and Rodgers, 1957). South of this point the sea floor and land are both calcareous and there are no streams to bring in detritus.

Ginsburg and Lowenstam (1958) described the important role that carpets of turtle grass, *Thalassia testudinum*, play in sedimentation in the shallow water around the Florida Keys. They hold a layer of water semimotionless over the bottom, allowing the deposition of fine sediment that otherwise would pass by. Rubbery mats of blue-green algae found as much as 6 feet below the low tide mark in the Florida-Bahamas area entrap individual sediment particles with their thick external sheath of mucilaginous cellulose. Their binding action is very rapid; in laboratory experiments they have reestablished a surface mat through as much as 4 mm of sediment in 24 hours. Lamination of sediment results from variable proportions of sediment and algae (Black, 1933; R. N. Ginsburg, in Rezak, 1957). Algal heads with characteristic internal structures are developed in this environment, but they are even more prominent at the borders of freshwater lakes in the interior of Andros Island.

Fairbank (1956) studied the detrital terrigenous material in the greater than 0.074 mm fraction of bottom samples taken from an area extending from the Mississippi River delta to the Dry Tortugas. Terrigenous material made up less than 10 percent of all samples taken more than 30 miles from shore, including the samples taken 100 miles out, which contained only 1 percent of such material. Gould and Stewart (1955) reported that quartz in the northeastern part of the Gulf of Mexico drops below 50 percent at depths greater than 30 feet, and in successively deeper zones it is replaced completely by shell sand and then by a sand made up mostly of algal remains. The algal sand extends beyond the break in slope. Calcareous biostromal deposits and a coarser-textured glauconitic foraminiferal ooze are accumulating atop isolated highs at the outer edge of the shelf in the northwestern part of the Gulf of Mexico (Greenman and LeBlanc, 1956).

BAHAMAN PLATFORMS

The Bahama Islands lie atop several platforms otherwise covered by water to a depth of only a few tens of feet. These platforms have been isolated from terrigenous sediment since early Cretaceous time, as shown by the 14,500 feet of pure carbonate deposits in a deep boring on Andros Island. Oolite and fine-grained carbonate sediments cover most of the area, for reefs are just getting started again after near-extinction by the Pleistocene rise in sea level (Newell, 1955).

Oolite sand is found near the bank edge underlying a belt of agitated water that is presumably losing CO_2 by agitation, heating, and photosynthetic uptake as it moves across the bank. These oolites give C^{14} dates less than 2,000 years and so cannot have been derived from the mainland (Newell and Rigby, 1957). The Bahaman reefs, on the other hand, grow successfully where they are protected from warm, hypersaline, turbid bank waters and have access to the cool, clear waters of the Tongue of the Ocean (Newell, 1951).

On the bank west of Andros Island the water flow, particularly from April to September, tends to create sluggishness, high evaporation rates, and high salinity that reaches a midbank high of 45‰ and a maximum of 46.5‰ along the shore at the western apex of the island (Cloud et al., in press). Fine-grained carbonate deposits containing large numbers of aragonite needles are found there. The 6 to

12 percent calcite in these sediments is partly material low in Mg, a detrital contribution from bedrock and shore, and partly solid solutions containing 11 to 19 mol percent MgCO_3 that increase in amount offshore and are probably of skeletal origin. Newell (1955) pointed out that the prominence of these deposits results from the absence of effective horizontal circulation; similar materials probably are forming on platforms elsewhere and being rather quickly swept out and dispersed through large areas of deeper water.

There has been much discussion about the origin of these fine-grained calcareous sediments. Lowenstam (1955) found that aragonite needles of the same habit and size as those in the muds west of Andros Island are secreted within certain of the calcareous algae and released by disaggregation after death. They are prevalent in Codiaceae and less frequent in Dasycladaceae, Nemalionaceae, and Chaetangiaceae. He showed a definite correlation between living areas of these forms and sediments containing aragonite needles at Jamaica, Bermuda, the Florida Keys, and the Bahamas. From occurrences of algae and aragonite needles at other places, Lowenstam concluded that the needles may be expected in quiet-water sediments wherever aragonite-needle secreting algae occur within equatorial shoal waters bounded by the 15° isotherms for the coldest month of the year.

Lowenstam and Epstein (1957) determined the $\text{O}^{18}/\text{O}^{16}$ and $\text{C}^{13}/\text{C}^{12}$ ratios of a number of aragonitic materials from the Great Bahama Bank in an effort to decide the origin of the sedimentary aragonite needles found in that area. The waters from which the various sample sets were collected varied in salinity and correspondingly had δO^{18} values ranging from about 1.6 to 3.2 relative to mean ocean water. Comparison of δO^{18} values for the entire group of samples was made possible by using corrected values that would have resulted if all the carbonates had been deposited in water having a value of $\delta\text{O}^{18} = 0$. On this basis, 23 algal aragonites had δO^{18} values ranging from -1.4 to -4.7, with an average of -3.1; 9 samples of sedimentary aragonite needles ranged from -2.4 to -3.2, average -2.7; 12 samples of oolites and grapestones ranged from -1.6 to -2.0, average -1.8. The significance of the average for algal aragonites is diminished somewhat by the fact that all algae were collected in May, eliminating the effect of annual temperature variation. The corresponding δC^{13} values are: algal aragonites, 0.1 to 5.9, average 3.8; sedimentary aragonite needles, 2.8 to 4.9, average 3.6; oolites and grapestones, 3.2 to 5.2, average 4.7. Both δO^{18} and δC^{13} values for the sedimentary aragonite needles, including samples of the material found above sea level on Yellow Cay which is contributing second-cycle material to present-day offshore muds, lie well within those of the algae, and the needles could have been derived from a mixture of different types of algae. The values for the oolites are narrowly restricted to one extremity of the algal range, making both an algal origin of oolites and the formation of sedimentary aragonite needles by oolite disaggregation quite unlikely. Lowenstam and Epstein concluded that any inorganic methods of formation of these sedimentary aragonite needles that can be postulated to explain their isotopic composition could not take place at the average temperature of the area and under equilibrium conditions.

Cloud et al. (in press) found that on the bank west of Andros Island, alkalinity varies inversely with chlorine content and salinity, indicating a condition running counter to simple concentration effects. Apparently the anions that determine alkalinity are being lost. Chief among these is bicarbonate, and the parallel deficiency in Ca^{++} indicates that CaCO_3 precipitation is taking place by some means, either purely physico-chemical, by organic skeletal growth, or as a result of precipitation following photosynthetic CO_2 withdrawal from the water. Cloud believed the first of these effects the most important. Local zones of water turbid with tiny aragonite

needles ("whittings") are occasionally encountered on the banks. The water in these zones is saltier, heavier, higher in Ca^{++} , and lower in alkalinity than normal bank water. Cloud believed that whittings are literally aragonite showers, and that the water composition within them is that to be expected for precipitation just begun.

The gross biochemical picture of these sediments involves the decomposition of organic matter, principally carbohydrate, with evolution of gas and a reduction in pH, generally below 7.8 and going down to 6.9 as a lower limit (the range in the overlying water is 8.02 to 8.15). The $\text{SO}_4^{=}/\text{Cl}^-$ ratios arrived at by chemical analysis remain essentially constant in both sediment and bank waters. Sulfate-reducing bacteria are rare, and Eh measurements of the sediment at the time of collection averaged zero, as compared with +0.32 for bank water. These results do not indicate the highly reducing environment characteristic of a high sulfate-reducing bacterial population, such as is responsible for the production of sulfide in most marine environments. However, iodine titrations of the calcareous mud indicate that some sulfate is being reduced; a total sulfite determination in a mud sample gave over 1000 ppm Na_2SO_3 or equivalent, whereas sulfide is present in amounts too small for mass spectrometer determination.

Alkalinity tends to run high in the sediment water. The fine grain size of the sediment hinders the flushing out of bacterially produced CO_2 and exchange with normal water, the pH decreases, and both Ca^{++} and alkalinity increase to high values. Should these waters move into higher pH levels, the increase in the $\text{CO}_3^{=}$ fraction of the alkalinity presumably would favor precipitation. Aragonitic induration of pellets and algal fragments, and aragonite cementation of grapestone clusters toward the bank margin indicate that CaCO_3 precipitation is taking place within the sediments.

Limy marine sediments such as those deposited in aerobic environments are commonly macerated and pelletized by worms, crustaceans, echinoids, and holothurians, because the sediments contain nutrient organic matter and are deposited slowly enough to allow prolonged contact with bottom dwellers (Moret, 1940; Twenhofel, 1942). The value for the rate of precipitation arrived at by Cloud et al., based upon computed rates of CaCO_3 precipitation and water exchange and upon C^{14} dating, is about 0.8 mm of wet sediment a year. At such rates, there is time for a major fraction of the sediment to pass through the organisms that feed on sediment (see Dapples, 1942). The measured pH within a holothurian before feeding is as low as 4.5 (Mayer, 1924), so significant amounts of CaCO_3 must be dissolved within these organisms, only to be excreted, mixed with sea water, and reprecipitated. The activity of mud-feeding organisms is shown clearly in North Atlantic deep-sea cores (Bramlette and Bradley, 1940) in which volcanic ash shards have been worked upward in diffuse arrangement from originally thin beds.

Although fecal pellets are quite susceptible to disaggregation, they may be preserved under favorable conditions. At least 90 percent of a sediment from an area in the northern extremity of Bimini lagoon is made up of fecal pellets from the gastropod *Batillaria minima* (Gmelin) that consist of a mucus-bound aggregation of silt-sized particles of CaCO_3 that hardens permanently on exposure during low spring tides (Kornicker and Purdy, 1957).

Fine sediments at one point pass down a gradient to form a submarine delta of limy ooze in deep Atlantic waters north of Eleuthera Island (Newell, 1955). Similar fans in a series to the north along the lower margin of the continental rise off the North American coast contain less and less carbonate (Ericson et al., 1955).

THE MEDITERRANEAN AREA

The Mediterranean Sea

The Mediterranean Sea, with a threshold of 1050 feet, does not have a stagnant bottom. Few large streams flow into it, and the amount of terrigenous detritus is consequently rather small.

Calcareous algal deposits and *Serpula*-reefs occur close to the northern and southern shores, but are more vigorous on the southern because there the water temperature is significantly higher (Gripp, 1958). A coccolith-rich deposit near Monaco contains 50 to 80 percent CaCO_3 (Bernard and Lecal-Schlauder, 1953), the sands and oozes of the open sea may contain as much as 46 percent (Bourcart, 1953), and oolite deposits on the southern shore more than 90 percent. Along the eastern part of the French Mediterranean coast, the zone of sediments richest in CaCO_3 is that of the shell sands from 30 and 60 meters depth, between coastal terrigenous sands and gravels and the muds that lie at greater depths (Nesteroff, 1959). Carbonate deposition is particularly vigorous along the coast east of Tunis because the current from the Atlantic, which cools Algerian coastal water, swings toward Sicily.

A small euxinic lake on the island of Mjlet near Dubrovnik, Yugoslavia, is connected to the Adriatic Sea by a passage only about 2.5 meters wide and 0.2 meters deep (Vuletic, 1953; Seibold, 1958). The fine-grained sediment in the deepest part is finely laminated, a light-colored layer and the adjacent dark one together averaging about 0.25 mm thick. The annual nature of the layering has been established by correlation with known datable events. The light-colored layers contain more than 60 percent CaCO_3 by dry weight, 1.5 percent MgCO_3 , and 0.7 percent Fe_2O_3 , and were formed in summer. The darker winter layers contain considerable quartz, organic matter, and pyrite, and only 30 to 50 percent CaCO_3 .

The Black Sea

The Black Sea has a threshold only 130 feet deep, and below the surface layer brought in by rivers the water is increasingly H_2S -bearing. The beds of the eastern and western deeps are varved and show characteristic light and dark laminations. The black laminations in particular are clayey and rich in organic matter and various forms of iron sulfides. A typical estimate for the varved sediment is 62 percent CaCO_3 , 2.5 percent iron sulfide, 31 percent terrigenous materials, 1 percent biogenous silica, 8 percent organic matter (Wolansky, 1933; Strakhov, 1951; Trask, 1939). Diatomaceous calcareous ooze forming in a small area in the western basin has from 20.7 to 60.7 percent CaCO_3 .

A considerable contribution of detrital carbonate is brought into the eastern pool by high-gradient rivers draining the Caucasus, and shell fields of high purity are extensive in shallower waters near Kerch and in the northwestern Black Sea.

During diagenesis, the interstitial water of the Black Sea sediments loses its marine character and is converted to a chloride-sodium-calcium water, for which Shishkina (1959) gives a partial analysis. The change in water composition in this sediment, rich in organic matter and CaCO_3 , is contrasted with the relative constancy of interstitial water composition for hundreds of thousands of years in Pacific Ocean sediments low in organic matter.

The Red Sea

The Red Sea, into which no permanent streams flow, has a maximum depth of 7200 feet, but a threshold of only 240 feet (Dunbar and Rodgers, 1957). The

bottom deposits are carbonate sediments largely of organic origin and containing up to 97 percent CaCO_3 . The suite of detrital minerals deposited in the northern Red Sea is the same everywhere, indicating mainly wind transportation of material from nearby areas of crystalline rocks (Shukri and Higazy, 1944b). The highest carbonate percentages are found for coarse, well sorted accumulations of skeletal material on shallow or sloping bottoms; organic material is more abundant in basins (Said, 1951; Shukri and Higazy, 1944a). The entire water column is warm, seldom dropping below 22°C at depth even in winter, and the salinity of $40^\circ/\text{oo}$ to $41^\circ/\text{oo}$ is among the highest recorded for any existing open sheet of water, so that it is surprising that chemically precipitated CaCO_3 is not more conspicuous (Said, 1951).

Patches of minute crystals of authigenic pyrite fill the hollow spaces of micro-organisms, especially foraminifera, in the sediments of the Gulf of Suez (Shukri and Higazy, 1944b). Decomposition of the organic matter is presumed to have furnished a reducing environment in which the pyrite formed.

The Persian Gulf

The Persian Gulf, although underlain by a long, narrow geosynclinal trough containing thick sediments and subordinate volcanics, is at present receiving carbonate-rich sediments with a predominantly resistant heavy mineral suite that are more typical of slow deposition on an aerobic foreland (see Emery, 1956; Houbolt, 1957). A small amount of the finest fraction of the terrigenous material brought in by the rivers at the head of the Gulf spreads out along the eastern side of the Gulf, along with contributions from the carbonate-rich, wind-borne dust described earlier and from torrents flowing during a few days of the year in otherwise dry watercourses. The " CaCO_3 " content of the sediments, measured from weight loss in HCl , ranges from 20 percent or less near the river mouths, to 57 to 65 percent for the marls in the central part of the Gulf, to virtually 100 percent in the shell sands east of the Qatar Peninsula. The average for the whole Gulf is about 80 percent.

Although there are limited areas of coral reefs and oyster reefs in the Gulf, and skeletal material, mainly molluscan, is accumulating everywhere except in the middle part, nearly half the carbonate is fine-grained material of undetermined origin. Fine fractions washed out of the calcarenites on shoals are transported southeastward to add to the local carbonate contribution in those somewhat deeper waters. Emery noted that sediments contain more than 85 percent carbonates in areas where salinity is greater than $40^\circ/\text{oo}$, but average only 60 percent for salinities between $38^\circ/\text{oo}$ and $39^\circ/\text{oo}$.

Warm saline water leaving the Gulf sinks below cold, entering water along the southwest side of the Strait of Hormuz at the south end of the Gulf, creating a zone of turbulence characterized by high nutrient values and abundant plankton production. This is also the principal area in which oolites occur. They are presumed to be forming now, for Wolf (1959) mentioned no oolite beds on Hormuz Island from which the oolites now in the Strait could have been derived.

High water temperatures and vigorous bacterial action prevent organic material from accumulating in substantial amounts. Emery gave a range of 0.031 to 0.201 percent organic N by dry weight of sediment, an average organic content of 1.7 percent, and a C/N ratio of 10.7. The high nitrogen value is from an area receiving organic debris swept in from the Strait of Hormuz. Houbolt (1957) gave a range of 0.063 to 0.176 percent for N, 0.2 to 1.2 percent for C, a C/N ratio of about 5 to 7.5 for the relatively organic-rich marly calcarenites in the central part of the Gulf, and a C/N ratio of about 5 to 2.9 for purer calcarenites and for lagoonal

muds near Doha. Pollen behaves as a hydrodynamically sorted detrital component in these sediments; about 225 (small) grains/gm of sediment are found in the marly calcarenites, less than 25 (large) grains/gm in the purer carbonates.

The less-than-1-micron fractions of these sediments examined by D. V. Bouma (*in* Houbolt, 1957) contained 5 to 20 percent montmorillonite, 20 to 40 percent illite, 5 to 20 percent kaolinite, and 35 to 60 percent calcite.

Small pyrite concretions are most common in the marly calcareous deposits of the deeper central parts of the Gulf. Many fecal pellets and shells of certain gastropods and foraminifera that occur in this area, including, especially, *Textularia* and Miliolidae among the latter, are full of black specks. These shells often have glauconitized centers and may have glauconitic infillings. The black specks are absent in the glauconitized shells. Microchemical analyses of three samples of black pellets and shells by C. R. Kolder (*in* Houbolt, 1957) showed 1.2 to 1.7 percent Fe, 2.3 to 2.5 percent Si, less than 0.2 percent N, and 0.086 to 0.188 percent organic carbon.

THE INDONESIAN ARCHIPELAGO

Globigerina ooze has only a limited distribution in the eastern part of the Indonesian Archipelago studied by the *Snellius* Expedition (Neeb, 1943) because of the abundant supply of volcanic and other terrigenous material that acts as a diluent and because of the CaCO_3 -dissolving power of strong currents present in many areas. Areas of highly calcareous ooze owe their existence to basins with shallow sills (for example, the Soeloe Sea) that limit exchange with adjacent bodies of water, to nearby limestone coasts or coral reefs that furnish carbonate terrigenous detritus, or to current winnowing of fines on ridge tops coupled with the presence of an intervening trough that catches most of the terrigenous detritus (for example, the Ceram-Timor outer arc). Local deposits of carbonate-rich coral sand are found around reefs.

Glauconite is most commonly found filling foraminiferal shells. Pyrite occurs in 62 percent of the *Globigerina* ooze samples examined, and a correlation between pyrite and organic matter is observed by Neeb. Samples with less than 0.05 percent organic N contain no pyrite, whereas those with more than 0.2 percent always contain pyrite. The organic N present in 14 *Globigerina* oozes and calcareous terrigenous muds containing an average of 63 percent CaCO_3 ranged from 0.025 to 0.19 percent (average, 0.085). Organic C in 10 of these samples ranged from 0.33 to 1.70 percent (average, 0.70).

SEDIMENTS OFF SOUTHERN CALIFORNIA

Carbonate sediments currently are being formed in some parts of the topographically complex region off southern California (Emery, 1960). CaCO_3 makes up about 80 percent of the coarse sediment of the tidal channels draining the marshes of Newport Bay, California, and there is one large area of shell sand on the mainland shelf. CaCO_3 content increases seaward in both shallow and deep water sediments as the percentage of shell fragments rises because of the progressively smaller detrital contribution from the mainland and offshore islands. Winnowing out of the fine fraction by currents in straits and on bank tops leaves a particularly carbonate-rich concentrate of larger particles of skeletal debris that, however, has a relatively low content of organic matter compared with that of the basins. Foraminiferal and molluscan sediments on bank tops average 56 percent CaCO_3 (166 analyses) and 0.8 percent organic matter (146 analyses), where percent organic matter = 17 (percent N) or 1.7 (percent organic C). Straits deposits contain an average of 60

percent CaCO_3 (50 analyses) and an estimated organic content of 0.5 percent (Emery, 1954). Highly calcareous coarse layers in some of the offshore basins are attributed to turbidity currents and, in at least one basin, contain a flood of augite like that found on bank tops (Emery and Rittenberg, 1952). *Globigerina* ooze, from a depth range averaging 11,000 feet, has 78 percent CaCO_3 (31 analyses) and 0.7 percent organic matter (19 samples) (Emery, 1954).

Emery and Rittenberg (1952) observed that sulfate is rapidly reduced to sulfide by bacteria in the sediments of offshore California basins, at some places disappearing within a depth of seven feet. This process results in negative Eh values and an increase of pyrite with depth. Pyrite forms within radiolarian shells, even when the sediment does not have a positive Eh, because of the local reducing conditions occasioned by the decomposition of a high concentration of organic matter. Although most of these materials are far from being carbonate sediments, a fair number of samples listed by Emery and Rittenberg contain as much as 40 percent carbonate. A similar relation of pyrite to diatom and foraminiferal shells was noted by Archanguelsky (1927) for Black Sea sediments.

In the sediments of the basins Emery and Rittenberg (1952) noted that both carbonate and N increase with small distances from shore, because of less dilution by terrigenous material. Farther out, slower rates of deposition permit more complete oxidation in the bacteriologically active surface layer of sediment, and N decreases even though carbonate continues to increase. *Globigerina* ooze has a very low N content. The amount of organic matter decreases rapidly in basin cores until the zero Eh level is reached (0 to 6 meters depth) and then decreases more slowly (Emery, 1960).

The more carbonate-rich sediments on shallow shelves and bank tops usually contain less than 10 ppm by dry weight of acetone-soluble chlorophyll derivatives calculated as pheophytin, whereas quantities in the basins are an order of magnitude greater (Orr et al., 1958). Destruction of organic matter, including that of the phytoplankton that are the main source of chlorophyll, is favored in this environment by high oxygen content, effective wave and tidal action that stirs and resuspends fine particles, a high bottom population of detritus feeders, and a slow rate of sediment accumulation.

The influence of topography on wave and current distribution and consequently on sediment composition also is shown at Todos Santos Bay, Baja California (Emery et al., 1957) where a coarse sediment containing large numbers of broken pelecypod shells analyzed 75 percent and more CaCO_3 . This material is found between the bay and the ocean on a ridge that receives very little detrital material. A similar very coarse sediment in the straits between Cedros Island and the mainland of Sebastian Viscaïno Bay contains an average of 60 percent CaCO_3 (Emery et al., 1957).

Redistribution of silica is already taking place in these sediments. Emery and Rittenberg (1952) found dissolved silica in concentrations up to 58 ppm in the interstitial water, much higher than those in the overlying sea water. "Amorphous silica" in siliceous tests, which were formed in sea water undersaturated with "amorphous silica," is apparently dissolving after death of the organism and cessation of metabolic processes (Siever, 1957). Russian workers quoted by Siever (Bruevich, 1953; Bezrukhov, 1955; Lisitsyn, 1955) also found relatively high concentrations of dissolved silica in interstitial waters of the Bering Sea and observed corroded and partially dissolved diatom shells in the sediments.

Glauconite and collophane occur together on bank tops and ridge crests where the overlying water is turbulent and oxygenated and the rate of sediment

accumulation is low. It is possible that within this environment the glauconite forms in micro-reducing environments within fecal pellets and foraminiferal and other tests. Some of it certainly does, for Emery (1960) described glauconite-containing foraminiferal shells in place at their proper depth range. Van Andel and Postma (1954) have recently described glauconite forming in a similar environment on an open, well oxygenated platform off the south coast of Trinidad.

Emery ascribed the phosphate formation to inorganic precipitation from the cool, upwelling deep water of the area. The water, rich in phosphate and other nutrients, undergoes an increase in temperature and pH (CO_2 loss) and a decrease in pressure on rising. Vigorous phytoplankton activity in the high-nutrient zone furnishes organic matter and some additional phosphate to the sediments. The theory of the inorganic precipitation of phosphate was first set forth in detail by Kazakov (1937, 1950) and apparently was realized independently by W. W. Rubey (see McKelvey, Swanson, and Sheldon, 1953, p. 56) and by Dietz et al. (1942).

THE PERU-CHILE TRENCH

Zen (1959) described a 4 cm-thick rhodochrosite-containing zone in the clayey mud of a core from the Peru-Chile Trench. The rhodochrosite, which consists of skeletal and subhedral crystals, was identified by X-ray diffraction, X-ray fluorescence, and optical measurements. In a restricted portion of one core, fine-grained dolomite is found as coatings 1 mm thick on the mud that forms the bulk of the core.

PELAGIC CARBONATE SEDIMENTS

Atlantic Ocean

Surface currents determine the distribution and number of organisms contributing calcareous tests to the bottom in the deep ocean, whereas the bottom currents and bottom topography, which may channel the currents, determine the rate of solution of tests falling through the water column (Pratje, 1939). Abundant data cited by Wattenberg (1927) showed that oxygen content decreases within a few hundred meters of the bottom, especially in the western Atlantic. The absolute values of oxygen concentration have, apparently, changed even since 1927. Preliminary examination of the data obtained in 1957 by the *Crawford* (Woods Hole Oceanographic Institution) compared with that obtained by the *Meteor* and the *Atlantis* some 30 years before shows little change in temperature and salinities but a significant loss of oxygen in deep water. It is thought that in neither polar region has it been cold enough in recent years to form water of sufficient density to replace the cold water now present in the deep oceans (Science, 1958).

The pelagic oozes locally contain numerous tests of pteropods but are principally made up of tests of pelagic foraminifera belonging to the families Globigerinidae and Globorotaliidae. The carbonate-rich *Globigerina* ooze of the Atlantic is cut off at 45 to 50° south latitude by the northern extension of ice-rafted glacial marine sediments and diatom ooze. Lisitzin (1959) described patches of bryozoan sediments of Recent age, containing more than 50 percent CaCO_3 , that occur in the zone of the ice-rafted sediments. The *Globigerina* ooze — red clay transition is a rather sharp one, effected by depth and local bottom current distribution. Thus, there is more red clay and blue mud on the west side of the South Atlantic than on the east because on the west the bottom current goes farther north before it crosses over the mid-Atlantic Ridge (Pratje, 1939).

Ericson (1959) summarized data indicating that the coarse crystallinity of the tests of planktonic foraminifera, compared with tests of the same species living in the euphotic zone, is characteristic of fully mature individuals and not a consequence of recrystallization or of the inorganic precipitation of calcite after the death of the organism.

Correns (1928) noted that constriction of the cross section of large, slow-moving currents where they flow across ridges increases their velocity enough to winnow out fine particles and increase the rate at which CO_2 , formed by the oxidation of organic matter, is swept away. Pratje (1939) found that clay fines had been removed from ridges in the South Atlantic by currents of intermediate depth, leaving calcareous oozes on the ridges as far as 35° south latitude.

Bramlette and Bradley (1940) noted that cores from topographic highs in the North Atlantic are more than usually stained by hydrous iron oxide and manganese oxide and contain no pyrite, indicating an oxidizing environment. Trask et al. (1942) attributed the low content of organic matter, only 0.2 to 0.3 percent, in the coarse, carbonate-rich sediments from these ridges to current winnowing of the buoyant organic material. Ericson et al. (1955) published underwater photographs of ripple marks on these rises, and isotopic data that show accumulation rates on the rises are much lower than those in deep water. The leeward concentration of fine-grained material swept off the Muir seamount ($33^\circ 42' \text{ N}$, $62^\circ 30' \text{ W}$) can be identified in cores (Ericson and Heezen, 1959); on the basis of limited information available from two cores, it appears that current direction, and the consequent direction of sediment drifting, shifted with climatic change.

Turbidity current deposits have been described (Ericson et al., 1952, 1955) in a number of cores from depths of more than 4000 fathoms on the flat abyssal plain of the Puerto Rico Trench and from more than 220 fathoms off the Bermuda Islands. The cores contain graded layers increasing in particle size and CaCO_3 content downward, in one case from 36 percent to 76 percent carbonate, and containing shallow-water foraminifera, particles of *Halimeda*, coarse vegetal detritus, and certain species of clams that must have lived in very shallow water. Absence of the occasional small teeth and rare benthonic foraminifera usually found in deep-sea clays indicates rapid deposition. These authors noted that the frequency of turbidity current deposits encountered in Atlantic cores is higher in sediments representing the rapid sedimentation of the glacial stages than in either older or younger deposits.

The carbonate content of the *Globigerina* oozes examined in North Atlantic deep-sea cores (Bramlette and Bradley, 1940) ranged from 46.8 to 90.3 wt percent, averaging 68.2 percent. Ericson and Wollin (1956) obtained CO_2 values equivalent to from 43.7 to 77.0 percent CaCO_3 in the foraminiferal lutites of cores A179-4 (off the southwest coast of Haiti) and A180-73 (midway between Brazil and Africa on the gently sloping flank of the mid-Atlantic Ridge). Both cores consisted of materials that appeared to have been deposited particle by particle. Biogenic carbonate in these samples is diluted by fine-grained terrigenous sediment from Africa and South America (see analysis 27, Part IV).

Oxygen-isotope determinations of paleotemperatures (Emiliani, 1955a), micropaleontological study of the vertical distribution of cold- and warm-water species (Ericson and Wollin, 1956b), and radiocarbon dating (Ericson et al., 1956) of core A180-74 from an equatorial portion of the mid-Atlantic Ridge establish that a rather abrupt change to a warmer climate took place about 11,000 years ago. Broecker et al. (1958) made carbonate analyses and further C^{14} measurements on less-than-74-micron size fractions from the same core and found that neither clay

nor carbonate deposition had been constant over the time span considered, and that the rate of deposition of both decreased markedly about 11,000 years ago. Core A172-6 from off Haiti was studied by Yalkovsky (1957) who found no correlation between paleotemperature and the rate of carbonate deposition.

Wangersky (1959) recently examined all four of the CaCO_3 -rich cores described above, A180-73, A180-74, A172-6, and A179-4. No apparent correlation was found between total percent CaCO_3 and paleotemperature, but the amount of fine-grained coccolith carbonate shows a negative correlation and the coarser foraminiferal carbonate a positive correlation with paleotemperature. Mg is inversely correlated with paleotemperature (correlation coefficient -0.61, significant at the 0.05 percent level), and a consideration of the SiO_2 analyses suggests that Mg is deposited chiefly in clays during interglacial periods and principally in carbonate, probably coccoliths, during the glacial periods.

The calculated Mg carbonate for 31 samples from North Atlantic deep-sea cores averages only 2.19 percent (Bramlette and Bradley, 1940). In only a few of the 20 precision analyses made was the Ca present insufficient to combine with all the CO_2 found, which suggests the presence of dolomite. Limestone and dolomitic limestone pebbles and granules are the most common rock types in the glacial marine deposits, have the least total carbonate (well under 50 percent), and contain the most MgO. Two fractions of almost pure foraminiferal shells from the North Atlantic cores (Bramlette and Bradley, 1940) analyzed by J. J. Fahey contained less than 0.01 percent SO_3 .

Phosphate nodules associated with greensand have been dredged from the Agulhas Bank, south of Africa, at depths of 400 to 1500 fathoms (Twenhofel, 1932).

Pacific Ocean

Bottom water introduced into the Pacific Ocean from the high southern latitudes contains 5.0 ml/l dissolved O_2 and has an in situ temperature of 0.9°C (Wooster and Volkmann, 1960). Property changes indicate a northward drift, and the deep water of the eastern Pacific, which has 3.4 ml/l dissolved O_2 and an in situ temperature of 1.6°C , is the most modified and presumably the oldest. Morita and ZoBell (1955) reported that red clays and *Globigerina*-ooze samples from cores in the open ocean are oxidizing at all core depths and at most depths contain an apparent preponderance of aerobic bacteria over anaerobic ones. This oxidizing environment is in direct contrast to the markedly reducing conditions that prevail in nearshore sediments of high organic content.

Calcareous oozes are extensive in the South Pacific but generally at less depth than in the Atlantic. Pacific pelagic samples contain 50 percent or more CaCO_3 above about 3500 meters; Atlantic samples reach that level above about 4900 meters (Revelle, 1944). Revelle et al. (1955) suggested that the difference may be related to differing rates of carbonate accumulation and thus differing periods available for corrosion, or to differing amounts of CO_2 derived from decomposing organic matter (Revelle, 1944). The larger Pacific Ocean has fewer large rivers and a smaller area of river drainage. Goldberg and Arrhenius (1958) noted that the concentration ranges observed for Mn, Cu, Ni, Co, Zn, Pb, Fe, and Ti in Atlantic pelagic sediments are lower than those for Pacific pelagic deposits. They assumed that the rate of deposition of marine deposits is inversely related to Mn content and thus concluded that accumulation rates are higher in the Atlantic.

The region of more than 75 percent carbonate content in the surface sediments of the east Pacific lies just south of the Equator but swings north at its

eastward end (Arrhenius, 1952). This distribution parallels the surface current pattern, for the equatorial countercurrent sends a branch northeastward and dissolves in a series of vortices as it passes over the East Pacific Ridge. Upwelling in the latter area results in high organic productivity, a plentiful supply of organic matter for the sediment, far-reaching dissolution of foraminiferal tests, and a consequently lowered CaCO_3 content in the sediment.

The rate at which Ti settles out in the east Pacific eupelagic area was found by Arrhenius (1952) and Arrhenius and Blomqvist (1956) to be practically constant. The C/N ratio of marine organic matter there is lower in clayey sediments than in highly calcareous ones, and organic N content is higher. A gradual decrease of organic N downward in cores that have essentially constant organic C contents indicates secondary decomposition of organic matter.

The unusually high Mn content of sediments of the East Pacific Ridge, compared with those of the eupelagic area to the west, indicates (Arrhenius, 1952) that Mn was introduced there by submarine weathering as well as from land. The P content on the ridge is unusually high, and the corrosion and peptization of radiolaria and diatoms is much more severe than in the eupelagic area. Some laminae on the ridge are strongly cemented by silica, indicating silica migration within the sediment. Such cementation does not occur in the eupelagic area, and its occurrence on the ridge may result from rising interstitial solutions heated at lower depths.

Revelle et al. (1955) showed that there are several types of CaCO_3 variation with depth in the Pacific: continuous high CaCO_3 , high surface CaCO_3 and lower CaCO_3 with depth, and low surface CaCO_3 and higher CaCO_3 with depth. Increased oceanic circulation during the Ice Age must have furnished a more abundant nutrient supply for plankton growth, but it also must have enhanced the dissolution of calcareous plankton tests settling to the ocean bottom. Thus the percentage of carbonate in the pelagic sediments at a given locality depends upon the relative importance of the two factors (Arrhenius, 1954), assuming that contributions of detrital minerals and minerals formed inorganically in the ocean remain essentially constant.

Siliceous skeletal remains commonly form more than 30 percent of Pacific calcareous oozes, a distinctly higher figure than is found for the Atlantic (see Correns, 1950). Goldberg and Arrhenius (1958) found a steep gradient in the silicon content of near-bottom water at all of the South Pacific stations they investigated, indicating a flow of dissolved silica from the bottom sediments back into the ocean. The contribution of eolian quartz from large arid continental areas is marked in pelagic sediments of the Pacific at lower and middle latitudes in the Northern Hemisphere, except in the region of the Hawaiian Islands where it is outweighed by an influx of basaltic pyroclastics (Goldberg and Arrhenius, 1958; Hamilton, 1957). The particle size range most frequently observed for the quartz shards and chips, 1 to 20 microns, is reasonable for eolian transport, as is the observed distribution pattern of the quartz when it is considered with regard to atmospheric wind fluxes and the location of arid regions on the continents (Rex and Goldberg, 1958).

Globigerina ooze of Eocene age on Sylvania Guyot, the seamount adjacent to Bikini Atoll in the Marshall Islands, and on Horizon Guyot 1500 miles to the east has been extensively phosphatized and encrusted with Mn oxides, indicating a marked diminution in the rate of sediment accumulation (Hamilton and Rex, 1959).

Areas of turbidity-current deposited graded beds occur in the bottoms of trenches off the northwest coast of North America.

HYPERSALINE LAGOONS

The northern portions of the Laguna Madre, a bay along the semiarid Texas coast separated from the open Gulf of Mexico by a wide barrier island, have a salinity about twice that of the Gulf (Rusnak and Shepard, 1957). Gypsum is precipitating on shallow flats, and aragonitic oolites are forming where waves break on the inner shore of the bay. Oyster reefs thrive in brackish water areas of the Laguna Madre.

The waters of the long, narrow Bocana de Virrila inlet on the arid Peruvian coast contain progressively less Ca^{++} and HCO_3^- and become steadily more saline toward the head of the inlet. The "white marls" being deposited in the seaward part of the inlet are presumably carbonates, as they are succeeded by gypsum and then by halite deposits lying under higher salinity water farther from the sea (see Morris and Dickey, 1957).



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